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14. ABSTRACT

Symposium U brought together scientists and engineers working on high efficiency thermal to electric energy conversion technologies to discuss the most recent progress in materials, current theoretical and experimental trends, characterization, and device fabrication. The symposium was designed to emphasize the multi-disciplinary nature (materials science, physics, chemistry and engineering) of the research needed to advance the state-of-the-art technology. Over 175 abstracts were received. This was more than any of the prior thermoelectrics MRS symposia and a strong testament to the continuing interest in this area of study.

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Symposium U held at the 2007 MRS Fall Meeting
Final Progress Report

Symposium U, "Thermoelectric Power Generation," held November 26–29 at the 2007 MRS Fall Meeting in Boston, Massachusetts, was the eighth in a series of thermoelectric materials research symposia related to new thermoelectric materials and devices [see MRS Proceedings volumes: 234, 478, 545, 626, 691, 793, 886]. In this symposium there were 135 contributed presentations including 11 invited talks and 63 posters. A steady and growing interest in the field of thermoelectric materials is evidenced by the continual increase in the number of submitted abstracts throughout the series of symposia. Even with the narrowed focus on thermoelectric power generation, this symposium was no exception having the highest number of contributions in the series.

The efficiency, η, of a thermoelectric power generator can be written as the product of a Carnot efficiency component, η_c, given as the ratio of the temperature gradient over the hot side temperature, and a thermoelectric component, η_{ZT}, such that $\eta = \eta_c \cdot \eta_{ZT}$. The thermoelectric component, η_{ZT}, is a function of the unitless figure of merit, ZT, and rapidly increases at low ZT values then asymptotically approaches a value of one in the limit. Higher efficiencies can therefore be achieved with large temperature gradients, and through improvements in ZT (commonly used materials have $ZT \approx 1$). This figure of merit is based on the material properties as $ZT = \alpha^2\sigma T/\kappa$, where α is the thermopower, σ the electrical conductivity, and κ is the thermal conductivity of the material. It is a challenging task to find materials with high electrical conductivity while simultaneously exhibiting high thermopower, and low thermal conductivity. Promising materials are often brittle and significant research in the processing of these materials is also of interest. Some results of current research in these areas are contained in these proceedings, and it is the hope of the organizers of this symposium that these proceedings will provide a concise reference for the current state of the field of thermoelectric materials research and development.

Within this symposium, there were sessions on nanocomposite materials including an excellent overview given by Millie Dresselhaus (MIT) on the use of "self assembled," and "force-engineered" nanocomposites in bulk samples. Jian He (Clemson) described the coating of pulverized *p*-type Bi_2Te_3 powders followed by hot pressing into bulk samples. Mercouri Kanatzidis (Northwestern U.) showed $ZT > 1.4$ for self assembled nanostructured PbTe-based bulk materials. George Nolas (U. of South Florida) described efforts in material systems including group IV clathrates, nanostructured chalcogenides, and antiflourite compounds and the use of powder processing techniques for the fabrication of bulk samples. Thallium telluride, and gallium telluride materials with extremely low thermal conductivity of below 0.5 (W/m·K) were presented by Shinsuke Yamanaka (Osaka U.). Theoretical studies of oxide thermoelectrics were presented by David Singh (ORNL) using conventional Boltzmann transport and showing the origin of the desired bandstructures coming from the bonding topology. Wataru Koshibae (Sendai National College of Technology) presented theoretical analysis on strongly correlated electron systems, and S.D. Mahanti (Michigan State U.) presented theoretical studies of the $AgPb_mSbTe_{m+2}$ material system. Mahanti showed self assembled nanostructuring in these materials can be understood through clustering and ordering of Ag, Sb, and Pb ions, and the temperature dependent electrical conductivity is dominated by the temperature dependence of the relaxation time rather than its energy dependence. Qiang Li (Brookhaven National Lab) described modeling and fabrication efforts toward materials with high power factors, and Holger Kleinke (U. of Waterloo) presented several new interesting compounds including $Mo_3(Sb,Te)_7$, $Nb_3(Sb,Te)_7$, and $Re_3(E,As)_7$ (with E = Si, Ge, Sn). Filling of the voids with nickel gave the compound $Ni_{0.06}Mo_3Sb_{5.4}Te_{1.6}$ as a degenerate *p*-type semiconductor that reaches ZT = 0.96 at 750°C. The symposium focused not only on the preparation and properties of new materials, but also included several talks on the processing of these new materials into devices, and the mechanical properties of thermoelectric compounds. In addition, the development status for the use of several advanced thermoelectric materials in radioisotope thermal generators for space applications was given

by Thierry Caillat (JPL). Continued interest in the area of thermoelectrics was evidenced by the number of outstanding presentations received, and the excellent level of attendance throughout the symposium.

The greatest returns come from investments in human capital through training and research of future scientists. As with previous thermoelectrics related symposia, there were a large number of graduate student presentations. Through the generous support of sponsors for this symposium, six graduate student oral presentation awards, and five graduate student poster awards were given. These students included:

Oral Presentations

Xiaofeng Qiu (Case Western Reserve University) "Synthesis and Characterization of Novel Thermoelectric Nanomaterials"

Bo Zhang (Clemson University) "PbTe Nanocomposites Fabricated by a Nano Surface Coating Technique"

Fei Ren (Michigan State University) "Mechanical Characterization of PbTe-based Thermoelectric Materials"

Vladimir Jovovic (Ohio State University) "Galvanomagnetic Measurements of Neodymium Doped Lead Telluride"

Matt Beekman (University of South Florida) "Synthesis and Characterization of Inorganic Clathrate-II Materials"

Joseph R. Sootsman (Northwestern University) "Transport Behavior, Thermal Conductivity Reduction, and Improved Thermoelectric Performance in the Composite System PbTe – Pb – Sb"

Poster Presentations

Ann I. Persson (University of Oregon) "Thermal Conductivity Measurements of Epitaxially Grown Nanowire Arrays Using TDTR"

Sabah Bux (University of California) "Synthesis and High Temperature Thermoelectric Properties of Nano Bulk Silicon and Silicon-Germanium Semiconductors"

Masataka Fukano (Tokyo University of Science) "Crystal Growth of Mg_2Si by the Vertical Bridgman Method and the Doping Effect of Bi and Al on Thermoelectric Characteristics"

Yoriko Mune (Nagoya University) "Origin of Giant Seebeck Coefficient for High Density 2DEGs Confined in the $SrTiO_3/SrTi_{0.8}Nb_{0.2}O_3$ Superlattices"

Yohei Oguni (Tokyo University of Science) "Formation of Transition-metal-based Ohmic Contacts to n-Mg_2Si by Plasma Activated Sintering"

The organizers are most grateful for the very gracious support of the Science and Technology Division of the Office of Naval Research, General Motors Corporation, Marlow Industries, Quantum Design Incorporated, Tellurex Corporation, ULVAC Technologies Incorporated, and the Materials Research Society. Their support enabled the large number of student awards and allowed for travel funds to help support contributing presenters.

Timothy P. Hogan
Jihui Yang
Ryoji Funahashi
Terry M. Tritt

April 2008

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Symposium U: Thermoelectric Power Generation

SYMPOSIUM U

2007 FALL MEETING
November 26-30
HYNES CONVENTION CENTER
BOSTON, MA

U: Thermoelectric Power Generation

November 26 - 29, 2007

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* Invited paper

SESSION U1: Nanocomposites I
Chair: Tim Hogan
Monday Morning, November 26, 2007
Room 311 (Hynes)

10:15 AM *U1.1
Low-dimensional and Nano-composite Thermoelectric Materials. Lidong Chen, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

Recent resurgence in thermoelectric (TE) materials research has led to a significant improvement of TE performance and development of some new TE materials designs and concepts. This review provides a summary of some effective techniques for improving TE performance through multi-level

microstructure control. A proven approach to elevate figure of merit is via formation of nanocomposites, in which nanophases are dispersed at grain boundaries or within grain. Acting as energy filter or scattering center, nanophases contribute to the increase of Seebeck coefficient and the reduction of thermal conductivity without much degradation of electrical conductivity. For anisotropic TE materials, textured microstructure favors to enhance TE performance along the certain direction. In addition, TE thin film assembled from one-dimensional nanotructured materials is presented as a promising TE film.

10:45 AM U1.2

Alkali Metal Hydrothermal Treatment ---- Fabricate a Beneficial Interface on p-type Bi2Te3 Thermoelectric Materials. Xiaohua Ji, Jian He, Zhe Su, Nick Gothard and Terry M Tritt; Department of Physics and Astronomy, Clemson University, Clemson, South Carolina.

Bi2Te3 based alloys have been known as one of the best room-temperature thermoelectric (TE) materials for decades. However, the thermoelectric performance of Bi2Te3 based alloys is sensitive to the inherent microstructure of the material: the pulverized system often exhibits an inferior figure of merit than that of the aligned ingot, due primarily to the inter-grain boundary scattering. So an important question may arise as to whether one can somehow fabricate a beneficial inter-grain boundary. In order to address this question, p-type Bi2Te3 is employed as a test-system in present work. Pulverized Bi0.4Sb1.6Te3 (p-type) powders with selected sizes were put into the autoclave and then hydrothermally treated, where the solution of various alkali metal (Li, Na, K, Rb, Cs) compounds were being used as reaction medium. After the treatment, the as-processed powders were removed, washed and dried, followed by hot pressing into pellet for further TE property measurements. The TE properties were found to be significantly improved as compared to the untreated reference sample. Extensive characterizations including X-ray/electron diffraction, TGA analysis, Raman / Fourier Transform Infrared Spectroscopy, electron microscopy, Rutherford back-scattering and Energy dispersive X-ray analysis were performed on the treated sample. The results revealed that a surface layer (from 10 nm to up to micron in thickness) exhibiting a combined crystalline/amorphous feature was formed on the original bare particles. This layer is believed to be the key factor in the improvement of TE properties of the p-type Bi0.4Sb1.6Te3 material. The synthesis technique will be discussed in detail while some results on the microscopic analysis and TE properties will be presented briefly.

11:00 AM U1.3

Synthesis and Characterization of Novel Thermoelectric Nanomaterials. Xiaofeng Qiu[1], Ian Steward[2], Jeffrey S. Dyck[2] and Clemens Burda[1]; [1]Chemistry, Case Western Reserve University, Cleveland, Ohio; [2]Physics, John Carroll University, University Heights, Ohio.

Nanostructured thermoelectric materials hold great promise in achieving efficient thermal-electric energy conversion. However, the difficulties in synthesizing and handling sub-100nm structures make nanoscale thermoelectrics a real challenge. Therefore, it is very important to develop methods that can provide thermoelectric nanomaterials as building blocks for the future high performance devices. Towards this end, we successfully developed a novel sonoelectrochemical method for the synthesis of Bi2Se3 heterostructure nanowires and PbTe nanorods, which are able to fine tune the size and shape of materials. Structural properties as determined by TEM will be presented. In order to test the transport properties of nanostructured thermoelectric materials, we also developed a chemical method to fabricate both nanostructured n-type Bi2Se3 and p-type PbSe thin films. The compositional and structural properties of the obtained films were characterized with XRD, XPS and SEM. Results from temperature dependent thermoelectric transport measurements showed large Seebeck coefficient for both Bi2Se3 and PbSe thin films. We will discuss key relationships among the synthetic parameters, sample composition, structure, and thermoelectric properties. This method shows a promising way to prepare nanostructured thermoelectric thin films and could potentially provide an attractive route toward fabricating better thermoelectric devices. References: 1.X. F. Qiu, C. Burda, R. L. Fu, L. Pu, H. Y. Chen, J. J. Zhu, "Heterostructured Bi2Se3 Nanowires with Periodic Phase Boundaries" J. Am. Chem. Soc. 2004, 126, 16276-16277. 2.X. F. Qiu, Y. B. Lou, A. C. S. Samia, A. Devados, J. D. Burgess, S. Dayal, and C. Burda, "PbTe Nanorods via Sonoelectrochemistry" Angew. Chem. Int. Ed. 2005, 44, 5855-5857. 3.X. F. Qiu, L. N. Austin, P. A. Muscarella, J. S. Dyck, C. Burda, "Nanostructured Bi2Se3 Films and Their Thermoelectric Transport Properties" Angew. Chem. Int. Ed. 2006, 45, 5656-5659.

11:15 AM U1.4

Thermoelectric Properties of Bi_2Te_3-based Nanocomposites. Nick Gothard, X. Ji, J. He and T. M. Tritt; Clemson University, Clemson, South Carolina.

Nanocomposites have been produced by incorporating thermoelectric nanoparticles into a matrix of bulk Bi_2Te_3 material via a hot pressing process. These nanocomposites have been examined by SEM and X-ray powder diffraction. The effects of the incorporation of a variety of nanoparticles upon the resulting thermoelectric properties such as the thermopower, electrical resistivity, thermal conductivity, etc., have been studied in these composites at room temperature and below. The details of the synthesis along with results of the microscopic analysis and thermoelectric properties will be discussed. The potential for improving the figure of merit within the Bi_2Te_3 system by this technique is considered.

11:30 AM U1.5

Synthesis and Thermoelectric Properties of Lead Chalcogenide Nanocomposites. Joshua Martin[1], Stevce Stefanoski[1], Lidong Chen[2] and George S. Nolas[1]; [1]Physics, University of South Florida, Tampa, Florida; [2]Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

Lead chalcogenide dimensional nanocomposites were prepared by densifying nanocrystals synthesized employing an alkaline aqueous solution-phase reaction. The nanocrystal synthesis procedure resulted in high product yields of over 2 g per batch. These nanocrystals were then subjected to Spark Plasma Sintering (SPS) for densification. Transport properties were evaluated through temperature dependent resistivity, Hall, Seebeck coefficient, and thermal conductivity measurements, indicating a strong sensitivity to stoichiometry, surface oxygen adsorption, and porosity. The results for these lead chalcogenide nanocomposites were compared to bulk polycrystalline lead chalcogenides with similar carrier concentrations.

11:45 AM U1.6

Thermoelectric Properties of Semiconducting Silicide Nanowires. Song Jin[1], Jeannine R. Szczezh[1], Feng Zhou[2] and Li Shi[3,2]; [1]University of Wisconsin-Madison, Madison, Wisconsin; [2]Materials Science and Engineering Program, Texas Materials Institute,, Materials Science and

Engineering Program, Texas Materials Institute,, Austin, Texas; [3]Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas.

Semiconducting silicides (e.g. $CrSi_2$, β-$FeSi_2$, $MnSi_{1.8}$, Mg_2Si) are promising thermoelectric materials. In addition to their respectable thermoelectric figure-of-merit (ZT up to 0.8), silicides have the advantages of low cost, excellent thermal stability and mechanical strength, and outstanding oxidation resistance, making them suitable for high temperature applications. We have developed general synthetic approaches to high quality single crystal nanowires of silicides to investigate their potential enhancement of thermoelectric properties due to the reduced nanoscale dimension and to explore their applications in thermoelectrics. We will specifically focus on the synthesis and structural characterization of nanowires of chromium disilicide ($CrSi_2$) prepared via a chemical vapor transport (CVT) method. This method complements the more versatile chemical vapor deposition (CVD) of metal carbonyl-silyl single source organometallic precursors we have developed. Structural characterization using electron microscopy, powder X-ray diffraction, and energy dispersive spectroscopy shows that these nanowires are hexagonal $CrSi_2$ single-crystal structures along the <001> growth axis, with diameters ranging from 20−300 nm and length up to 100 μm. The Seebeck coefficient, electrical conductivity, and thermal conductivity of individual $CrSi_2$ nanowires were characterized using a suspended microdevice and correlated with the crystal structure and growth direction obtained by transmission electron microscopy on the same nanowires. The obtained thermoelectric figure of merit of the nanowires was close to 0.1 and comparable to the bulk values. This combined Seebeck coefficient and electrical conductivity measurements also provide an effective approach to probing the Fermi level, carrier concentration and mobility in nanowires. We will also discuss our recent results of silicide nanowires of complex Novotny chimney ladder phases and our progress in using individual nanostructures combined well-defined structural characterization to conclusively investigate the complex thermoelectric behaviors of these silicide materials.

SESSION U2: Nanocomposites II and Theory
Chairs: S.D. (Bhanu) Mahanti and Terry Tritt
Monday Afternoon, November 26, 2007
Room 311 (Hynes)

1:30 PM *U2.1
New Opportunities in Existing Thermoelectric Materials: Interface Engineering in Pulverized p-Bi_2Te_3 System. Jian He, Xiaohua Ji, Zhe Su, Nick Gothard and Terry M. Tritt; Physics, Clemson University, Clemson, South Carolina.

Grain boundary scattering provides an avenue by which to effectively lower the thermal conductivity in pulverized thermoelectric materials, however, the "bare" inter-grain boundary often simultaneously degrades the electrical conductivity and thermopower. Thus a controlled inter-grain boundary would be very beneficial in order to improve the thermoelectric performance of the system. But the question is how to engineer such a boundary. In this talk we present a proof-of-principle investigation on the pulverized p-Bi_2Te_3 ($Bi_{0.4}Sb_{1.6}Te_3$) system by means of electrical resistivity, thermopower, thermal conductivity, specific heat, Hall coefficient, Raman/Infrared spectroscopy, X-ray/electron diffraction, electron microscopy and compositional analysis. Utilizing the alkaline hydrothermal treatment and nano-coating techniques recently developed at Clemson, we fabricate a thin layer on the surface of fine p-Bi_2Te_3 grains. The interface layer, ~ few tens nm thick and formed right at the inter-grain boundary in a hotpress-densified sample, enabled us to "decouple" and individually optimize the various thermoelectric properties. As a result, the hydrothermally treated and pulverized sample possessed ZT values comparable to those of a commercial ingot but with a better so called "compatibility factor" as well as better mechanical properties. In view of the concept of material design, this process helps achieve a new level of control as a tuning parameter with which to optimize the figure of merit ZT and compatibility factor. In principle, this strategy can be readily applied to other existing thermoelectric materials. This presentation will focus on the resulting thermoelectric properties and microscopic analysis and the synthesis techniques will be discussed in detail elsewhere.

2:00 PM U2.2
Effect of In-Situ Hydrogen Annealing on the Thermoelectric Properties of Individual Bismuth Telluride Nanowires. Anastassios Mavrokefalos[1], Michael Thompson Pettes[1], Li Shi[1], Wei Wang[2] and Xiaoguang Li[2]; [1]Mechanical Engineering, University of Texas at Austin, Austin, Texas; [2]Department of Physics, University of Science and Technology of China, Hefei, China.

Several theoretical studies suggested that Bi-based and III-V nanowire structures may possess enhanced thermoelectric figure of merit, ZT. It was found in our earlier measurements employing a suspended microdevice that the thermoelectric properties of individual bismuth telluride, InSb, and $CrSi_2$ nanowires are largely influenced by the crystalline quality, chemical composition and surface roughness of the nanowires. In addition, a major problem for thermoelectric measurements of individual nanowires especially bismuth telluride nanowires is the presence of a stable native oxide that prohibits electrical contact to be made directly to the nanowires. Focused electron or ion beam induced deposition of Pt on the nanowire was used in our previous work to make electrical contact to the nanowire. Care was needed to prevent the nanowire from being contaminated by ions present during the Pt deposition process. Furthermore, it has been suggested that the presence of the surface oxide or surface contamination can result in high surface charge state densities that can dominate the intrinsic transport properties of nanowire and thin film thermoelectric materials. In fact, it was found that annealing in a hydrogen environment can significantly enhance the thermoelectric properties of bismuth telluride films. In this work, we investigate the effect of in situ hydrogen annealing on the thermoelectric properties of individual bismuth telluride nanowires. The thermoelectric measurement method is based on an improved design of our microfabricated suspended device. The current measurement does not require Pt deposition on the nanowire for making electrical contact. Instead, it was found that ohmic contact between the nanowire and the underlying pre-patterned Pt electrodes on the suspended devices can be made by annealing the nanowire at about 480 K while hydrogen is flown into the evacuated sample space of a cryostat. Our measurement results show that that the thermal and electrical conductances and ZT of the nanowires are increased upon hydrogen annealing. In addition, both the contact thermal and electrical resistances are eliminated from the measured thermal conductivity, electrical conductivity, or Seebeck coefficient by using a unique four-probe thermoelectric measurement method. Transmission Electron Microscopy (TEM) and Energy Dispersion Spectroscopy (EDS) measurements are performed on the same nanowires assembled on the suspended device so as to correlate the structural characteristics to the measured thermoelectric properties of the nanowires. High resolution TEM results reveal highly crystalline structure of the hydrogen-annealed bismuth telluride nanowires.

2:15 PM U2.3
Synthesis and Thermoelectric Properties of High-purity Single-crystal InSb Nanowires. Feng Zhou[1], Jae Hun Seol[2], Yong Lee[2], Li Shi[2,1] and Qi Laura Ye[3]; [1]Texas Materials Institute, University of Texas at Austin, Austin, Texas; [2]Mechanical Engineering, University of Texas at Austin,

Austin, Texas; [3]NASA Ames Research Center, Moffett Field, California.

Indium antimonide (InSb) is a narrow bandgap semiconductor with one of the smallest effective mass values among semiconductors and very high mobility. It is commonly used in infrared detectors and magnetic field sensors. The thermoelectric properties of bulk InSb crystals have been characterized by Yamaguchi et al. in the 10-723 K temperature range, with highest figure of merit (ZT) of 0.6 found at 673 K [1]. A theoretical calculation by Mingo has predicted that quantum confinement of electrons and diffuse phonon-surface scattering in InSb nanowires can result in enhanced ZT compared to the bulk value [2, 3]. Ye et al. has developed a vapor-liquid-solid (VLS) method to synthesize single crystal InSb nanowires. In an previous measurement, we observed that the obtained VLS InSb nanowires possess higher electrical conductivity and lower Seebeck coefficient than bulk crystals, most probably due to tellurium or oxygen impurities in the nanowire [4]. In this work the impurity concentration in the VLS InSb nanowires is minimized by using pure InSb wafers as source materials for VLS growth in high vacuum environment. The crystal structure and chemical composition of the obtained nanowires are analyzed using High Resolution Transmission Electron Microscopy (HRTEM) and Energy Dispersive X-ray Spectroscopy (EDAX). Temperature-dependant thermopower and electrical conductance are probed using a nanofabricated device where a top gate and substrate back gate voltage can be used to tune the Fermi level of the system via the field effect. Experiments are conducted to investigate the effect of in situ hydrogen annealing and surface passivation on the thermoelectric properties of the InSb nanowires. [1] S. Yamaguchi, T. Matsumoto, J. Yamazaki, N. Kaiwa, and A. Yamamoto, "Thermoelectric properties and figure of merit of a Te-doped InSb bulk single crystal," Applied Physics Letters, vol. 87, Nov 2005. [2] N. Mingo, "Thermoelectric figure of merit and maximum power factor in III--V semiconductor nanowires," Applied Physics Letters, vol. 84, pp. 2652-2654, 2004. [3] N. Mingo, "Thermoelectric figure of merit and maximum power factor in III-V semiconductor nanowires (vol 84, pg 2652, 2004)," Applied Physics Letters, vol. 88, pp. -, Apr 3 2006. [4] J. H. Seol, A. L. Moore, S. K. Saha, F. Zhou, L. Shi, Q. L. Ye, R. Scheffler, N. Mingo, and T. Yamada, "Measurement and analysis of thermopower and electrical conductivity of an indium antimonide nanowire from a vapor-liquid-solid method," Journal of Applied Physics, vol. 101, pp. 023706-6, 2007.

2:30 PM *U2.4
Using Nano-composites to Enhance ZT. Mildred Dresselhaus, EECS and Physics, MIT, Cambridge, Massachusetts.

The concept of using self assembled nano-composites to enhance the thermoelectric figure of merit relative to bulk materials is presented in general terms. Specific application is made to the Si-Ge system for use at high temperature for space vehicle propulsion applications. The scientific advantages of the nano-composite approach for the simultaneous increase in the power factor and decrease of the thermal conductivity are emphasized along with the practical advantages of having bulk samples for property measurements and an easy method for the of scale-up of nanostructured building blocks into bulk quantities of material for device fabrication.

3:30 PM *U2.5
Oxide Thermoelectrics. David J Singh, Materials Science and Technlogy Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

NaxCoO2 is a fascinating material displaying a complex phase diagram and showing unprecedented properties. These include superconductivity upon hydration, apparent proximity to magnetic quantum critical points and high thermoelectric performance at metallic carrier densities. This high thermoelectric performance is remarkable as it was long held that neither oxides nor high carrier density metals could be good thermoelectrics. Furthermore, since the discovery of the thermoelectric properties of NaxCoO2 a decade ago, there are still no other examples of high performance thermoelectric oxides. Here, the problem of oxide thermoelectricity is discussed starting with NaxCoO2 within the context of electronic structure calculations and Boltzmann transport theory. These calculations suggest that there may well be other oxide thermoelectrics and suggest directions for identifying them. Some candidate materials are discussed.

4:00 PM U2.6
An Investigation of Sodium Ordering in NaxCoO2 (x ≧ 0.50) by Density Functional Theory. Ying Shirley Meng, Yoyo Hinuma and Gerbrand Ceder; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Understanding the remarkable thermoelectric properties and interesting electronic/magnetic phenomena in P2-NaxCoO2 requires a detailed understanding of the structures at various sodium concentrations where sodium and vacancy order at finite temperature, which can couple strongly with the electronic structure. Using first principles electronic structure methods within the GGA and GGA+U approximations we find that Na ordering is determined by a competition between Na site energies difference and Na-Na repulsion. In addition the Co-Na interlayer interaction when charge localization occurs can facilitate the lock-in of certain ordering patterns of Na-Vacancy at simple fraction fillings. We will compare and contrast the stable ordering schemes obtained in this work with available experimental observations. Our work shows excellent agreement with experiments, in contrast to the previous DFT studies, in addition we predict a series of new ground states at concentration 0.60 to 0.71.

4:15 PM U2.7
Large Thermoelectric Power Generated by the van Hove Singularity of Two-dimensional Triangular Lattice. Tsunehiro Takeuchi, EcoTopia Science Institute, Nagoya University, Nagoya, Japan.

Recently, layered cobalt oxides, such as NaxCoO2, Bi2Sr2Co2O9, and Ca3Co4O9, were found to simultaneously possess large thermoelectric power and metallic electrical conduction. Those properties are two of the three necessities of practical thermoelectric materials. The layered cobalt oxides, therefore, were widely considered as one of the promising candidates for the thermoelectric materials in the next generation. Surprisingly, the carrier concentration of these materials were distributed over 10^(21)~10^(22) cm^(-3), which values are considered as those of metallic phases which generally possess very small thermoelectric power less than 10 μV/K. Thus a large number of attentions have been focused on the mechanism leading to the large thermoelectric power exceeding 100 μV/K with the large carrier concentration. In our resent studies, we performed high-resolution angle resolved photoemission spectroscopy measurements on these layered cobalt oxides and investigated the energy-momentum dispersion near the Fermi level (EF) in detail. By using the experimentally determined electronic structure and the Bloch-Boltzmann theory, we found that the large thermoelectric power with metallic conduction of the layered cobalt oxides was brought about by the Boltzmann-type electrical conduction with a unique spectral conductivity characterized by the large peak just below EF in associated with the van Hove singularity (vHs) of the two-dimensional system. More recently, however, we realized that even though a large peak in the electronic density of states is generated by the vHs, the layered copper oxides of two-dimensionally spanned square lattice have a very small peak in the spectral conductivity and consequently possess relatively small magnitude in their thermoelectric power. In order to investigate the origin of the large vHs peak in the spectral conductivity of

the layered cobalt oxides, we employed, in this study, simple tight-binding simulations for several systems of different symmetry and calculated spectral conductivity within the rough assumption of a constant mean free path. As a result of the simulations, the very important role of the two-dimensionally spanned triangular lattice leading to a large peak in the spectral conductivity and consequently to a large magnitude in thermoelectric power was clearly revealed. In the presentation, the results obtained by the simulations will be explained in detail together with some typical examples of the two-dimensional triangular lattice possessing a large thermoelectric power.

4:30 PM U2.8
Defect Clustering and Nanostructure Formation in PbTe-based Bulk Thermoelectrics. Khang Hoang and Subhendra D Mahanti; Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan.

Lead chalcogenides (PbTe, PbSe, and PbS) are IV-VI narrow band-gap semiconductors whose studies over several decades has been motivated by their importance in infrared detectors, light-emitting devices, infrared lasers, photovoltaics, and high temperature thermoelectrics. PbTe in particular is the end-compound of several high performance high temperature thermoelectrics such as $AgPb_mSbTe_{2+m}$ [1] and $Na_{1-x}Pb_mSb_yTe_{2+m}$ [2]. These quaternaries are found to have enhanced thermoelectric figure of merit (compared to PbTe), due to the nanostructuring, which helps in lowering the lattice thermal conductivity and possibly enhancing the thermopower [1-2]. In this work we systematically study defect clustering in PbTe using density functional theory and supercell models. The defects being considered are (but not limited to) Na, K, Ag, Sb, Bi, and vacancies. Our energetic studies show that many defect pairs are stabilized when the two defects in a pair are either the nearest or the next-nearest neighbors in the PbTe lattice, which can help explain the nanostructuring found in various PbTe-based systems. Comparisons with similar defect cluster calculations in SnTe and GeTe will be made. We also study the electronic structure as a function of the relative distance between the two defects in a pair. Work partially supported by ONR-MURI. 1. K.-F. Hsu et al., Science 303, 818 (2004). 2. P. Poudeu et al., Angew. Chem. Int. Ed. 45, 3835 (2006).

4:45 PM U2.9
Disorder Creates Band Gap in (Pb,Sn)Te Alloys. Xing Gao and Murray S. Daw; Dept. of Physics & Astronomy, Clemson University, Clemson, South Carolina.

The PbTe, SnTe and their alloys are one of the commercial thermoelectric materials nowadays. The efforts to enhance its figure of merit have been extensively undertaking by doping rare-earth atoms, creating nano-structures in it, and so on. Furthermore, the electronic structure of Sn-doped PbTe is fundamentally interesting because of the so-called band inversion in its two end members, PbTe and SnTe [1,2]. Although, the electronic structure of these two compounds and their analogies have been intensively studied by first-principles calculations, to our best knowledge, there are no direct first-principles calculations of the band gap evolution through the full range of alloying. We report a study of the electronic structure of this material through the full range of alloy content, combining SQS [3] and LDA. Our results show that disorder plays an important role in the electronic structure of this alloy. The calculated results by taking account of the short-range disorder are in good agreement with experimental results. [1] Dimmock, Melngailis, and Strauss, Phys. Rev. Lett. 16, 1193 (1966). [2] Tung, and Cohen, Phys. Rev. 180, 823 (1969). [3] Wei and Zunger, Phys. Rev. B 55, 13605 (1997). This work is supported by DOE-EPSCoR.

SESSION U3: Poster Session
Monday Evening, November 26, 2007
8:00 PM
Exhibition Hall D (Hynes)

U3.1
Abstract Withdrawn

U3.2
Thermal Conductivity Measurements of Epitaxially Grown Nanowire Arrays using TDTR. Ann I Persson[1,3], Yee K Koh[2], Heiner Linke[1], Lars Samuelson[3] and David Cahill[2]; [1]Physics Department/Materials Science Institute, University of Oregon, Eugene, Oregon; [2]Department of Material Science and Engineering, University of Illinois, Urbana, Illinois; [3]Solid State Physics, Lund University, Lund, Sweden.

Nanowires are suggested to be suitable for high-efficiency thermoelectric materials. Their one-dimensional nature result in a sharply peaked electronic density of states, predicted to enhance the power factor, and in confinement effects on the phonon transport, predicted to lead to a lowered lattice thermal conductivity [1]. We have investigated the thermal conductivity of highly ordered InAs nanowire arrays embedded in PMMA (polymethyl methacrylate) and present here a new approach for measuring the thermal conductivity of the technologically relevant case of nanowire arrays, using time-domain thermoreflectance (TDTR) [2]. TDTR has proved to be a very powerful method for characterizing the thermal transport properties of a wide variety of materials and here we apply TDTR for the first time to vertically aligned nanowires. The nanowires are arranged in arrays, where each array contains nanowires uniform in diameter and length and positioned in an ordered pattern. This well-controlled structure therefore enables us to extract also the thermal conductivity of a single InAs nanowire. The nanowires are grown with chemical beam epitaxy (CBE) and are epitaxially nucleated and positioned using lithographically defined Au discs as seed particles. The nanowires grow in the (111) direction, perpendicular to the substrate surface, and their diameters are defined by the Au discs. The fabrication is described in more details in Jensen et al. [3]. By changing the lithography parameters both the size and the position of the Au discs can be altered, which allows us to create arrays with nanowires of different diameters and with different filling factor (fraction of the matrix that consists of nanowires, where the matrix in this case consists of PMMA and nanowires). We report the fabrication of uniform nanowire arrays and the use of TDTR to measure the thermal conductivity of vertically aligned nanowires. We also present results of measurements on arrays with different filling factors, containing nanowires with different diameter and different length, showing that the thermal conductivity of InAs nanowires is clearly suppressed relative to the bulk value. [1] L. D. Hicks, M. S. Dresselhaus, Phys. Rev. B 47 (2003) 16 631 [2] R. M. Costescu, M. A. Wall, D. G. Cahill, Phys. Rev. B 67 (2003) 054302. [3] L. E. Jensen, M. T. Björk, S. Jeppesen, A. I. Persson, B. J. Ohlsson, L. Samuelson, Nano Letters 4 (2004) 1961.

U3.3
Sub 10 nm Diameter Bi Nanowires Grown in ALD Modified Alumina Membrane. Lee Jongmin, Ulrich Goesele and Kornelius Nielsch; Max-Planck Institute of Microstructurephysics, Halle, Germany.

Thermoelectric effects involve the conversion between thermal and electrical energy and provide a method for heating and cooling materials. Thermoelectric bismuth nanowires were fabricated in a porous anodic alumina (PAA) membrane by pulsed electrodeposition. The self-organized PAA was prepared by 2nd step anodization process in 0.3M sulfuric acid and the pore diameter reached ca. 20 nm as-prepared. The pore diameter was reduced to sub 10 nm by using the Atomic Layer Deposition (ALD) in order to increase the thermoelectric figure of merit. Thermoelectric Figure of Merit (FOM) is strongly influenced by the diameter of nanowire, which was theoretically reported previously. FOM of Bi is increased significantly from 20 nm of diameter due to semimetal-semiconductor transition. After preparation the PAA in sulfuric acid, ALD was performed using Tri-methyl aluminum (TMA) and water (H2O) as precursors for the deposition of aluminum oxide (Al2O3) inside PAA. The pore diameter is varied at 20, 15, 10 and 5 nm depending on the number of ALD cycles. Bi nanowires were subsequently fabricated by pulsed electrodeposition in dimethylsulfoxide (DMSO) with bismuth chloride as an electrolyte under inert atmosphere. This process was performed at 130°C for the purpose of enhancing the Bi nanowire crystallinity as well as inhibiting the hydrogen evolution. Thermal conductivity and electrical conductivity are characterized with 3-omega system and 4-point probe system, where the metal wire is connected by e-beam lithography.

U3.4

Study of Nanostructured Thermoelectric Materials Using Integrated TEM-STM System. X. T. Jia[1], Y. C. Lan[2], Z. F. Ren[2], G. Chen[3] and M. S. Dresselhaus[4]; [1]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Physics, Boston College, Chestnut Hill, Massachusetts; [3]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [4]Department of Physics and Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nanostructured thermoelectric materials - nanowires, nanobelts and bulk materials - have attracted lots of interest in recent years, due to their enhanced performance regarding their thermoelectric figure of merit. However, because of equipment limitations, little work has been done on combining the structural behavior with transport measurement of these materials simultaneously. With an integrated TEM-STM system, we studied the structural behavior and transport properties of various nanostructured thermoelectric materials. We present results of these measurements and the physical reasoning behind these effects on the thermoelectric figure of merit. These results have implications on further directions to be taken for improvement of these thermoelectric materials. *Support for this work was provided by NSF-NIRT Grant number CBET-05-06830.

U3.5

Thermopower Measurements of Arrays of Small Diameter (13-60 nm) Bi Nanowires. Tito E. Huber, Ajibola Adeyeye and Tosin Odunfa; Chemistry, Howard University, Washington, District of Columbia.

Because of the increased density of states arising from quantum confinement, it is anticipated that quantum wires will exhibit superior thermoelectric properties and therefore high thermal-to-electric conversion efficiency. Bismuth is a model system for this study. Recently, angle-resolved photoemission spectroscopy (ARPES) studies have shown that Bi supports surface states that have not been considered in current models of quantum confinement. The surface states appear due to spin-orbit interaction, a feature of many thermoelectric materials. Studies of the Fermi surface, employing the Shubnikov-de Haas (SdH) method, in arrays of 30-nm to 80-nm bismuth nanowires partially corroborates ARPES findings. Measurements of the thermopower of nanowire array samples is challenging due to the small size of the samples. Still, our measurements of the thermopower of 60-nm Bi nanowires presented at the 2006 International Conference on Thermoelectrics indicate that n-type surface carriers dominate over the quantum-confined electrons and holes for T< 30 K. Assuming the model of diffusing thermopower, in smaller diameter nanowires the surface effects should be stronger and the temperature range over which the surface effects dominate should extend to higher temperatures. We report on measurements of the thermopower of arrays of 18-nm and 35-nm nanowires to test this model.

U3.6

Laser-assisted Synthesis and Optical Properties of Bismuth Nanorods. Jason Reppert, Rahul Rao, Malcolm Skove, Jian He, Terry Tritt and Apparao Rao; Clemson University, Clemson, South Carolina.

Infrared absorption, temperature-dependent electrical resistance and magneto-resistance measurements of Bi nanowires (diameter < 200 nm) prepared using the alumina-template method confirmed the existence of a semimetal-semiconductor phase transition. We report the synthesis of ~10 nm diameter Bi nanorods using a pulsed laser vaporization method. The high resolution transmission electron microscopy images of our Bi nanorods show a crystalline Bi core oriented along <012> direction, and coated with a thin amorphous Bi2O3 layer. The infrared absorption and the surface plasmon peaks in our Bi nanorods are blue-shifted in energy when compared to the corresponding spectra in bulk Bi.

U3.7

Mechanical Alloying Synthesis of $K_2Bi_8Se_{13}$ - type Solid Solutions Nikolaos Toumpas[1], Theodora Kyratsi[1], Euripides Hatzikraniotis[2], Andreas Tsiappos[1], Eleni Pavlidou[2], Konstantinos M. Paraskevopoulos[2], Duck Young Chung[4] and Mercouri G. Kanatzidis[3,4]; [1]Mechanical & Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus; [2]Department of Physics, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece; [3]Department of Chemistry, Northwestern University, Evanston, 60208, Illinois; [4]Materials Science Division, Argonne National Laboratory, Argonne, 60439, Illinois.

Solid solutions of β-$K_2Bi_{8-x}Sb_xSe_{13}$ are interesting series of materials for thermoelectric investigations due to their very low thermal conductivity and highly anisotropic electrical properties. On the other hand, powder technology is an advantageous approach on synthesis and processing of thermoelectric materials due to its features such as good mechanical properties, easy shaping, low temperatures, mass production, etc In this work, we aimed to synthesize solid solutions of β-$K_2Bi_{8-x}Sb_xSe_{13}$ type materials using powder techniques. The synthesis was based on mechanical alloying as well as sintering procedures. The products were studied in terms of structural features, composition and purity in order to find the conditions that lead to pure materials using powder x-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. Their thermoelectric properties (Seebeck coefficient, electrical conductivity) as well as IR reflectivity were also investigated. The results are compared with materials prepared from the melt.

U3.8

Impact of Nanoscale Substructures on the Thermoelectric Properties of AgPbmSbTe2+m. Qing Jie[1], Juan Zhou[1], Lijun Wu[1], Jincheng Zheng[1], Yimei Zhu[1], Qiang Li[1] and Jihui Yang[2]; [1]Condensed Matter Physics and Materials Science, Brookhaven National Lab, Upton, New York; [2]Materials and Processes Lab, GM R&D Center, Warren, Michigan.

We report a coordinated study of the thermoelectric and structural properties of AgPbmSbTe2+m (LAST-m) compounds in both single crystals and polycrystalline samples, in order to understand the impact of nanoscale substructures on the thermoelectric properties of LAST-m system. Analytical transmission electron microscopy (TEM) was used to obtain the structure information, while quantitative electron diffraction was used to explore the charge distribution. The ability for quantitative electron diffraction to probe nm-scale area is particularly useful in the studies of electronic structure of LAST-m compounds. Bulk thermoelectric properties were studied by direct transport measurements, and were compared with the infrared optical spectroscopy measurements of the same samples probing the electron and phonon dynamics. Evolution of nanoscale substructure and matrix materials as a function of temperature up to the melting point was investigated by in-situ TEM. We will discuss in detail the correlation between the thermoelectric properties and nanostructure of this class of materials at various temperatures.

U3.9

Structural Studies of GeTe-AgSbTe2 Alloys. Claudia J. Rawn[1], Bryan Chakoumakos[1], Jeff Sharp[2], Alan Thompson[2] and Pat Gilbert[2]; [1]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Materials R&D, Marlow Industries, Dallas, Texas.

GeTe, a small bandgap semiconductor that has native p-type defects due to Ge vacancies, is an important constituent in the thermoelectric material known as "TAGS" [1]. TAGS is an acronym for alloys of GeTe with AgSbTe2, and compositions are normally designated as TAGS-x, where x is the fraction of GeTe. TAGS-85 is the most important with regard to applications, and there also is commercial interest in TAGS-80. The crystal structure of GeTe1+δ has a composition-dependent phase transformation at a temperature ranging from 430 °C (δ = 0) to ~ 400 °C (δ = 0.02) [2]. The high temperature form is cubic. The low temperature form is rhombohedral for δ < 0.01, as is the case for good thermoelectric performance. Addition of AgSbTe2 shifts the phase transformation to lower temperatures, and one of the goals of this work is a systematic study of the dependence of transformation temperature on the parameter x. In addition to TAGS, there are other Ag-containing tellurides that are of interest as thermoelectric materials. These include LAST (PbTe + AgSbTe2), compositions in the Tl-Ag-Te ternary system, and Ag2Te. We present results on phase transformations and associated instabilities in TAGS compositions in the range of 60-85 at.% GeTe, and on the atomic displacement parameter of Ag in TAGS and other materials. [1] E. A. Skrabek and D. S. Trimmer, "Properties of the General TAGS System," in CRC Handbook of Thermoelectrics, ed. D. M. Rowe (CRC Press, Boca Raton, FL, 1995), pp. 267-275. [2] Ge-Te phase diagram, in Moffatt's Handbook of Binary Phase Diagrams, ed. J. H. Westbrook (Genium Publ. Corp., Schenectady, NY, 1995).

U3.10

Lanthanum Telluride: A Refractory Thermoelectric Material by Mechanical Alloying. Andrew May[1], Jeffrey Snyder[1] and Jean-Pierre Fleurial[2]; [1]California Institute of Technology, Pasadena, California; [2]Jet Propulsion Laboratory, Pasadena, California.

Lanthanum telluride demonstrates significant potential as an n-type material for high temperature thermoelectric application. The phase of interest is the cubic Th_3P_4 structure, which exists for compositions $La_{3-x}Te_4$ with $0 \le x \le ⅓$. Mechanical alloying is utilized to synthesize the refractory compound at room temperature. The TE properties of various compositions ($0<x<0.3$) are examined, and zT > 1 is obtained at 1000°C for several compositions. When x = ⅓, one-ninth of lanthanum atoms are vacant and the system is a charge balanced insulator. As lanthanum vacancies are filled, free electrons are introduced and a maximum carrier concentration of approximately $4.5{*}10^{21} cm^{-3}$ is expected for x = 0. TE properties vary as expected with the change in carrier concentration. Rare-earth chalcogenides of the Th_3P_4 structure thus offer an interesting inspection of the carrier concentration dependence of key TE properties. A two-band model characterizes the carrier concentration dependence and allows the system to be optimized for TE application. This analysis also provides insights into why lanthanum telluride is a zT>1 material and provides a framework for predicting the behavior of this and other TE systems.

U3.11

Thermoelectric Properties of the Pseudo-binary PbTe-Sb_2Te_3 Composites with Lamellar Structure at Nanometer Scale. Teruyuki Ikeda[1], Eric S. Toberer[1], Vilupanur A. Ravi[2], Sossina M. Haile[1] and G. Jeffrey Snyder[1]; [1]Materials Science, California Institute of Technology, Pasadena, California; [2]Department of Chemical and Materials Engineering, California State Polytechnic University, Pomona, California.

Recently, it has been recognized that thin film materials with nanometer scale features such as superlattice or quantum dots show dramatically improved thermoelectric properties. This is largely due to enhanced phonon scattering resulting in reduced thermal conductivity. For practical use for thermoelectric devices, bulk materials are desired, permitting easy handling, simple fabrication processes, relatively lower contact resistances and so on. In this research, a self-assembled bulk composite in the PbTe-Sb_2Te_3 system with the microstructure in nanometer scale was fabricated and the thermoelectric properties were investigated. So far, it has been shown that an intermediate phase $Pb_2Sb_6Te_{11}$ appears at the composition close to the eutectic composition (~10.5 at.% Pb) in the pseudo-binary system of PbTe and Sb_2Te_3 by a solidification process. Since this phase is metastable, the $Pb_2Sb_6Te_{11}$ phase decomposes into two immiscible thermoelectric materials, PbTe and Sb_2Te_3, by heat treatments at high temperatures, forming nanosized lamellar structure. In this work, the thermoelectric properties such as thermal and electrical conductivities were examined as functions of annealing time and temperature. The time dependence of the fraction transformed and the inter-lamellar spacing was also determined. In addition, in-situ measurements of these physical properties were performed. It has been found that the thermal conductivity decreases with decreasing inter-lamellar spacing. This is due to the reduction of the phonon part of the thermal conductivity.

U3.12

Effects of Tellurium and Thallium Doping on the Thermoelectric Properties of InSb. Zhe Su, Jian He, Daniel Thompson, Xiaohua Ji and Terry

M. Tritt; Physics, Clemson University, Clemson, South Carolina.

InSb is a promising candidate for thermoelectric applications in the intermediate temperature regime (500 K - 700 K). Single crystalline and polycrystalline Tellurium- and Thallium-doped InSb have been grown and characterized by means of resistivity, thermopower, thermal conductivity, and Hall coefficient measurements. The effects of Tellurium- and Thallium doping on the thermoelectric properties have been investigated, with the focus on lowering the thermal conductivity while preserving the high power factor in the InSb material.

U3.13

Elastic Moduli of Lead Telluride as a Function of Temperature. Fei Ren[1], Jennifer E Ni[1], Eldon D Case[1], Joe Sootsman[2], Mercouri G Kanatzidis[2], Edgar Lara-curzio[3] and Rosa M Trejo[3]; [1]Chem. Eng. and Materials Science, Michigan State University, East Lansing, Michigan; [2]Department of Chemistry, Northwestern University, Evanston, Illinois; [3]High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Lead telluride (PbTe) is one of the established thermoelectric (TE) materials. Some doped PbTe compounds show superior TE properties, which is of great interest in the TE community in recent years. Although the elastic moduli of single crystal PbTe were reported in 1960's, these characterizations were limited to room temperatures or below. There is little mechanical property reported on PbTe at high temperatures except a recent study of internal friction and relative shear modulus as functions of temperature by torsion pendulum method. In our study, we utilize resonant ultrasound spectroscopy (RUS) to characterize the elastic moduli as a function of temperature for polycrystalline PbTe materials fabricated by both the Bridgman method and quenching method. Young's modulus decreases with increasing temperature and exhibits a linear temperature dependence between room temperature and ~ 800 K. Our high temperature Young's modulus shows an excellent agreement when compared to the aggregate Young's modulus values in literature that were calculated from single crystal elastic constants for p-type PbTe single crystals. In addition to the Young's modulus, we also report the temperature dependence for shear modulus and Poisson's ratio.

U3.14

Systematic Investigation of Thermoelectric Materials: Substitution effect of Bi on the AgxPb18MTe20 (M = Bi, Sb) (x = 1, 0.86, 0.7). Mi-kyung Han[1], Huijun Kong[2], Ctirad Uher[2], Daniel Bilc[4], Mercouri G. Kanatzidis[1] and Subhendra D. Mahanti[3]; [1]Chemistry, Northwestern University, Evanston, Illinois; [2]Department of Physics, University of Michigan, Ann Arbor, Michigan; [3]Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan; [4]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

We have performed systematic investigation of the AgxPb18MTe20 (M = Bi, Sb) (x = 1, 0.86, 0.7) system to study the substitution effect of Bi in the system. Detailed charge transport data including electrical conductivity, Seebeck coefficient, Hall coefficient and thermal conductivity will be presented. In both systems, the electrical conductivity nearly keeps same values, while the Seebeck coefficient decreases dramatically by substituting Sb with Bi. The larger Seebeck coefficient of AgPb18SbTe20 is attributed to the resonance state at the conduction band. High resolution TEM images of both samples revealed that all systems contain compositional fluctuations at the nanoscopic level and are nanostructured. Compared to the lattice thermal conductivity of PbTe, that of AgPb18BiTe20 is substantially reduced. The lattice thermal conductivity of the Bi analog, however, is higher than that of AgPb18SbTe20 because of the decrease in the degree of mass fluctuation between the nanostructures and the matrix. As a result the dimensionless figure of merit ZT of AgxPb18MTe20 (M = Bi) is found to be smaller than that of AgxPb18MTe20 (M = Sb).

U3.15

Thermoelectric Properties of Nanostructured $(Pb_{1-m}Sn_mTe)_{1-x}(PbS)_x$ with Pb and Sb Precipitates. Steven N. Girard[1], Joe R. Sootsman[1], John Androulakis[2], Chia-Her Lin[2] and Mercouri G. Kanatzidis[1]; [1]Chemistry, Northwestern University, Evanston, Illinois; [2]Chemistry, Michigan State University, East Lansing, Michigan.

Nanostructuring achieved through spinodal decomposition and nucleation and growth in the thermoelectric material $(Pb_{1-m}Sn_mTe)_{1-x}(PbS)_x$ at m=0.05, x=0.04, 0.08, 0.16 will be presented as a method to obtain enhanced figures of merit. These systems are not solid solutions, but rather phase separate into distinct nanoscale PbTe and PbS regions as revealed by HRTEM. These nanoscale features help scatter phonons while allowing unaltered flow of charge carriers. We will compare and contrast the effectiveness of spinodal decomposition versus nucleation and growth in acoustic phonon scattering. Recently it has been demonstrated that precipitates of Pb and Sb can significantly alter charge carrier dynamics in PbTe. In this work, we report the thermoelectric properties of the $(Pb_{0.95}Sn_{0.05}Te)_{1-x}(PbS)_x$ system with excess concentrations of Pb and Sb. Electrical and thermal measurements will investigate transport properties. Scanning and high-resolution transmission electron microscopy will be used to determine the micro- and nanostructure of these new systems, and possibly understand the role of spinodal decomposition, nucleation and growth, and matrix encapsulation in achieving high efficiency thermoelectric materials.

U3.16

Investigation of Cubic PbS/AgSbS$_2$ System for Thermoelectric Applications. Duck-Young Chung[1], Iliya Todorov[1] and Mercouri Kanatzidis[1,2]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [2]Department of Chemistry, Northwestern University, Evanston, Illinois.

The PbS-based cubic system combines a number of attractive features for thermoelectric investigations. First, they possess highly symmetric cubic structures and similar favorable electronic band structures to those of PbTe-based materials. Second, they possess high melting points around 1400 K. Third, they are composed of readily available and abundant elements and finally they are much less investigated as thermoelectric materials compared to PbTe. Therefore, we have initiated investigations of the fundamental physical properties of not only PbS but a representative quaternary cubic system, PbS/AgSbS$_2$, as candidates for high ZT thermoelectric materials for solar thermal power generation. We will present the new cubic system including PbS and AgSbS$_2$ with respect to their synthesis, characterization, thermoelectric properties and possible chemical manipulation to control the properties. The crystal structure, lattice parameters, energy gaps and preliminary charge transport properties of selected members of this family will be presented.

U3.17

Estimation of Thermoelectric Property of FeVAl using Bloch Boltzmann Equation Based on First Principle Band Calculation. Hiroki Funashima and Noriaki Hamada; Department of Physics, Tokyo University of Science, noda, Japan.

Heusler and Half-Heusler arroy phases are among the best known intermetallic thermoelectric material.The crystal structure of Fe2VAl is Full Heusler phase(Space group is Fm-3m). Electric resistivity of Fe2VAl has temperature dependency likely semiconductor. We carried out Full-Potentail Linear Augumented Planewave(FLAPW) method within the Local Density Approximation(LDA)/LDA+U for full-Heusler Fe2VAl and applied Bloch-Boltzmann theory to electronic structure which we calculated to estimate thermoelectric properties (Seebeck coefficient , Electric conductivity and Powerfactor). Conductivity tensor is estimated by using electronic structure, assuming that relaxation time is independent of the wave vector and band index(constant relaxation time approximation). We report temperature dependency and carrier concentration dependency of thermoelectric properties quantitatively. In this study it calculates while original band energy is maintained according to the dope quantity of the carrier making use of the virtual crystal approximation. To calculate thermoelectric properties(electric conductivity, Seebeck coefficient), it is necessary to calculate electric structure order 10^-3$(Ry.). Because, in thermoelectric phenomena, in particular thermoelectric cooling-heating case, the temperature variation is order few dozen(K). In general band calculation, number of sampling point is less than few thousand. But it is too few to calculate accurately electric structure. To calculate detailed electric structure accurately(order 10^-3 Ry.), it is necessary to calculate enormous number of sampling k-point in Brilliouin zone. But, it is very hard to calculate such an enormous k-point using with ab-initio calculation. Thus we have interpolated k-point data from FLAPW band calculation data analytically on the basis of group theory. We used periodic and non-periodic cubic spline to interpolated E-k data over irreducible Brillouin zone. To integrate constant-energy surface to calculate thermoelectric property, we used tetrahedron method. Fe2VAl is knonw for strong correlated electron system. Thus we carried out LDA+U. Within LDA+U, our theorical thermoelectric properties in our calculation corresponded with experimental data. We calculated thermoelectric properties based on Bloch-Boltzmann theory, however, in generally speaking, its scheme is questionable for strong correlated electron system. Empirically, in spite of theoretical limit, we can obtain much valiant information from Bloch-Boltzmann scheme calculation, and we discuss about theoretical limit.

U3.18

Modeling the Electrical and Thermal Properties of Thermoelectric Materials. Austin Minnich, Daryoosh Vashaee and Gang Chen; Mechanical Engineering, MIT, Cambridge, Massachusetts.

In recent years several new approaches to designing thermoelectric materials have caused researchers to reexamine other materials previously thought unsuitable for thermoelectrics. Materials such as GaAs and InSb, while not currently used as thermoelectrics, could prove to be efficient thermoelectrics if prepared properly. To aid in this materials search we have developed a code which numerically calculates the electrical and thermal properties of many non-standard materials using the Boltzmann equation under the relaxation time approximation. The code incorporates a variety of scattering mechanisms and is capable of calculating properties over a wide range of temperatures and doping concentrations. Since lattice thermal conductivity can be reduced using the nanocomposite approach, we focus on characterizing materials by their electrical properties. We show that several materials have promising power factors and could serve as efficient thermoelectrics.

U3.19

The Electronic Structure Study of Sb2Te3 with Doping Elements from 1A to 7A by the Ab initio Method. Ming-Hong Chiueh and Shan-Haw Chiou; Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan.

We investigated the influence of the doping elements from 1A to 7A on Sb2Te3 crystal with performing first-principles calculations with the projector-augmented wave method and plane wave basis set. The formation energy and DOS were studied by substituting Sb and Te sites of Sb2Te3 with 1A to 7A elements. The calculation results show Be, Ca, Sr, Ba, B, Al and 4A and 5A elements substitute Sb or Te site to form p-type while the F substitutes Te site to form n-type.

U3.20

Temperature - Concentration Phase Diagram from First Principles Calculations in P2-NaxCoO2. Yoyo Hinuma, Ying Shirley Meng and Gerbrand Ceder; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The unusual electronic properties of NaxCoO2 are attracting considerable interest in recent years. At high sodium content, the system displays unusually strong thermoelectric effect and a low metallic resistance1. In this study, we present a temperature - concentration phase diagram for NaxCoO2 (0.5 <= x <= 1) obtained by combining Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA) with the cluster expansion technique and Monte Carlo simulation. In comparison we will also present the results obtained from the GGA with Hubbard U correction (GGA+U), which forces the charges on Co to completely localize, forming Co3+ and Co4+ cations unlike in the GGA in which no distinct Co3+ and Co4+ cations form. We will discuss the key interactions that determine the ground states and the order/disorder transition temperatures of these states, which may be important for understanding the thermoelectric properties of these mixed valence oxides. References: 1 I. Terasaki, Y. Sasago, and K. Uchinokura, Physical Review B 56, 12685 (1997).

U3.21

Theoretical Study of Phase Diagrams in $CoSb_3$-based Skutterudites. Xun Shi[1,2], Jihui Yang[2], Wenqing Zhang[3], Lidong Chen[3] and Ctirad Uher[1]; [1]Physics, University of Michigan, Ann Arbor, Michigan; [2]Materials and Processes Laboratory, General Motors R&D Center, Warren, Michigan; [3]State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai, China.

Skutterudites are among the most important thermoelectric materials for power generation in medium temperature ranges. We studied the thermodynamic stabilities of $CoSb_3$-based skutterudites by a plane-wave density functional method. A schematic phase diagram for single filled-skutterudites containing both impurity and pure $CoSb_3$ is obtained by taking into account of the configurational entropy contribution at different temperatures. We also studied the phase diagrams of skutterudite solid solutions made by alloying at the Co site of $CoSb_3$ skutterudite structure by density functional theory. A limited solid solubility is observed for $Ir_xCo_{1-x}Sb_3$ and $Rh_xCo_{1-x}Sb_3$ solid solutions, showing good agreement with

experimental reports. Our calculations show that $Ir_xRh_{1-x}Sb_3$ solid solutions and partial filled skutterudites are compounds with ordered structure rather than random solid solutions.

U3.22
Abstract Withdrawn

SESSION U4: Chalcogenides
Chairs: Lidong Chen and George Nolas
Tuesday Morning, November 27, 2007
Room 311 (Hynes)

8:30 AM U4.1
Melt Spinning Preparation of Bismuth Telluride and Partially Alloying with IV-VI Compounds for Thermoelectric Application. Harald Paul Boettner[1], Dirk Gustav Ebling[1], Alexandre Jacquot[1], Uta Kuehn[2] and Juergen Schmidt[3]; [1]Thermoelectric Systems, Fraunhofer Institute for Physical Measuremnt Techniques, Freiburg, Germany; [2]Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, Dresden, Germany; [3]Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung IFAM, Dresden, Germany.

Bismuth telluride and its alloys is known as the best thermoelectric semiconductor for room temperature application.One promising approach to improve thermoelectrical properties are nanocomposite materials with lower thermal conductivities and therefore higher ZT-values. Melt spinning, originally developed for rapid cooling of metal liquids, is used to develop material, that requires extremely high cooling rates in order to form metallic glasses or nanocomposites. Here we will report on the evolution of the thermoelectric material parameters like thermal and electrical conductivity, and the Seebeck coefficient in dependence on the fabrication and doping of the base material comparing the properties as prepared to different post-annealing processes. As far as the melt spinning process is concerned parameters like the rotation speed, extrusion pressure, casting temperature, distance nozzle to cooling wheel, pressure and kind of gas were varied. Crystalline, textured flakes of some 10μm thickness and areas ~30mm2 were achieved. Before and after post-annealing processes the flakes were structurally characterized by SEM, XRD and TEM and they could also be analysed for the Seebeck-coefficient and Hall-effect properties. Beside the intrinsic p- and n-doping the material was alloyed with up to 0.5% lead telluride to influence the thermoelectric properties by a tentative nanocomposite, see also the phase diagram respectively. The resulting flakes were also structurally characterized and analysed to about 600 K for the thermoelectric properties. Melt spinning is only capable to produce small and thin ribbon shaped specimens. This limits melt spinning for V2-VI3-materials currently to the manufacturing of academic specimens. Therefore in addition the spark plasma sintering (SPS)-technique was used to compress a few grams of the flakes to specimens which were suitable to determine the thermal conductivity of the melt spinning material. In addition the influence of the SPS-procedure was studied with respect to the thermoelectric properties of the material.

8:45 AM U4.2
Theory of Enhancement of Thermoelectric Properties of Materials with Nanoinclusions: Application to Pb_{1+x}Te. Sergey Faleev, Sandia National Laboratories, Livermore, California.

We present a theoretical model, based on the Boltzmann Transport Equation in relaxation time approximation, for description of the Seebeck coefficient and electrical conductivity for a PbTe system with Pb nanoinclusions. The effect of nanoinclusions has been taken into account by considering the electron scattering on the Schottky potential of the metal-semiconductor boundary of Pb islands. Both Born approximation and exact solution of the Schrödinger equation have been applied to calculate the scattering probability and it was found that Born approximation is applicable for small island radiuses or large electron concentration. The model predicts an increase of the Seebeck coefficient because the relaxation time due to scattering on the Pb islands has stronger energy dependence compared to the relaxation time for bulk PbTe. We demonstrated that the model can be applied to maximize the power factor by choosing an optimal radius of the the Pb islands and/or optimal concentration of the islands. The results for electron mobility and Seebeck coefficient calculated by our model are in qualitative agreement with recent experimental data. Nevertheless the experiments with more control on the geometry of scattering centers should be performed in order to quantitatively verify the validity of present model.

9:00 AM *U4.3
Nanostructured LAST and PbTe-based Thermoelectrics for Power Generation. Mercouri G. Kanatzidis[1], Tim Hogan[3], Ctirad Uher[2], Elson Case[4], Harold Schock[5], Pierre F. P. Poudeu[1], Mi-Kyoung Han[1], Hui-J. Kong[2], Adam Downey[3], Jonathan D'Angelo[3], Chun-I Wu[3], Rei Fen[4] and Edward Timm[5]; [1]Department of Chemistry, Northwestern University, Evanston, Illinois; [2]Department of Physics, University of Michigan, Ann Arbor, Michigan; [3]Department of Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; [4]Department of Chemical Engineering, Michigan State University, East Lansing, Michigan; [5]Department of Mechanical Engineering, Michigan State University, East Lansing, Michigan.

There is a strong incentive to develop thermoelectric materials for power generation with a vastly improved thermoelectric performance. Research in this area is expected to teach us how to design and prepare advanced bulk inexpensive nanostructured thermoelectric materials. Recently we have reported a number of novel PbTe-based materials with substantially enhanced figures of merit including AgPb18+xSbTe20 (LAST-18), NaPb20+xSbTe22 (SALT-20), AgPb18-nSnnSbTe20 (LASTT), PbTe-Sb and PbTe-PbS. All these systems are characterized by a strong tendency to nano-segregate into well defined nanostructured entities. The mechanism of nanostructuring appears to be either spinodal decomposition or nucleation and growth. These mechanisms results in coherent and semi-coherent nanometer sized inclusions in a PbTe matrix which can serve as sites for scattering of acoustic phonons thereby lowering the lattice thermal conductivity. The expectations for enhanced power factor and greatly reduced thermal conductivity in suitably chosen systems will be discussed. We will present fundamental scientific information regarding the influence of nanostructures on TE properties. We will also the challenges associated with processing these materials and our efforts to improve them via a variety of processing techniques. Results on the scaleup of LAST-18 and LASTT for the fabrication of TE modules will be presented.

9:30 AM U4.4

Mechanical Characterization of PbTe-based Thermoelectric Materials. Fei Ren[1], Bradley D Hall[1], Jennifer E Ni[1], Eldon D Case[1], Joe Sootsman[2], Mercouri G Kanatzidis[2], Edgar Lara-curzio[3], Rosa M Trejo[3] and Edward J Timm[4]; [1]Chem. Eng. and Materials Science, Michigan State University, East Lansing, Michigan; [2]Department of Chemistry, Northwestern University, Evanston, Illinois; [3]High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [4]Department of Mechanical Engineering, Michigan State University, East Lansing, Michigan.

PbTe-based thermoelectric (TE) materials exhibit promising thermoelectric properties and have potential applications in waste heat recovery from sources such as truck engines and shipboard engines. TE components designed for these applications will be subject to mechanical/thermal loading and vibration as a result from in-service conditions, including mechanical vibration, mechanical and/or thermal cycling, and thermal shock. In the current study, we present and discuss the mechanical properties of several PbTe-based compositions with different dopants and processing methods, including n-type and p-type specimens fabricated both by casting and by powder processing. Room temperature hardness and Young's modulus are studied by Vickers indentation and nanoindentation while fracture strength is obtained by biaxial flexure testing. Temperature dependent elastic moduli, including Young's modulus and Poisson's ratio are studied via resonant ultrasound spectroscopy (RUS).

9:45 AM U4.5

Phase Separation in Bulk Thermoelectric Alloys based on $AgPb_mSbTe_{2+m}$. Douglas L. Medlin, M. Hekmaty, A. Morales, M. Homer, M. Clift and J. D. Sugar; Sandia National Laboratories, Livermore, California.

Recent work in the literature has reported a high thermoelectric figure-of-merit for some compositions within the general formula of $AgPb_mSbTe_{2+m}$ (e.g. Hsu et al, Science 2004). This high performance has been attributed to the formation of nanoscale clusters thought to be rich in Ag and Sb. To better understand how such a nanostructure forms, we have synthesized a series of alloys based on this general formula and have investigated the structural evolution of these materials using transmission electron microscopy (TEM), x-ray diffraction, and electron microprobe measurements. For sufficiently high Ag and Sb concentrations, we find a two-phase microstructure composed of both fine-scale (~10-20 nm diameter) precipitates, which are rich in Ag and Sb, and larger scale (~100 nm and larger) lamellae of alternating Pb-rich and Ag/Sb-rich material. Fine-scale energy dispersive x-ray spectroscopy (EDXS) measurements in the TEM and larger-scale electron microprobe measurements show that the Ag and Sb concentrations track each other and are anticorrelated with the Pb concentration while the Te concentration remains fixed. This result is consistent with the notion that, in these materials, silver and antimony substitute for Pb in the crystal structure and have a tendency to cluster. This idea is further supported by electron diffraction measurements showing that both phases are topotactically aligned and are consistent with a cubic, rock-salt-type structure. The Ag/Sb-rich phase possesses a 4% smaller lattice parameter than the Pb-rich phase--a somewhat smaller difference than that between pure PbTe and $AgSbTe_2$ (6%). This misfit leads to dense arrays of dislocations at the lead-rich and antimony/silver-rich phase boundaries.

We will discuss our microstructural results in the context of the existing body of literature on phase stability in the Pb-Te-Ag-Sb system with the goal of identifying the conditions for obtaining an optimal internal nanostructure and assessing the conditions under which this structure will remain stable.
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States DOE-NNSA under contract DE-AC04-94AL85000.

10:30 AM *U4.6

Atomic Ordering, Electronic Structure, and Transport Properties of LAST-m Systems. Subhendra D. Mahanti, Physics and Astronomy, Michigan State University, East Lansing, Michigan.

In recent years, LAST-m (AgPb_mSbTe_m+2) and related materials have emerged as potential high performance high temperature thermoelectrics.[1] These compounds are obtained by starting from PbTe, a well-known high temperature thermoelectric, and replacing a pair of divalent Pb2+ ions by a combination of a monovalent (Ag1+, Na1+, K1+ etc) and a trivalent (Sb3+) ion. One example is LAST-18. When appropriately doped, it gives a value of the thermoelectric figure of merit, ZT~1.7 near T=600-700K. A major reason for this large ZT is the low lattice thermal conductivity caused by the presence of nanostructures associated with the ordering of Ag, Sb, and Pb ions. These nanostructures scatter phonons efficiently. It is also believed that nanostructures can lead to increased thermopower by manipulating the electronic density of states near the Fermi energy.[2,3]In this talk I will discuss the possible origin of this atomic ordering[4,5] and how the presence of these nanostructures can affect the electronic properties of LAST-m compounds[6]. The physics of gap/pseudogap formation in the end member of this series, AgSbTe2, itself an excellent thermoelectric, will be explained.[7] Finally, I will discuss the transport properties of PbTe and LAST-m systems, focusing on the energy and temperature dependence of the transport function and how they impact on the temperature dependence of the electrical conductivity, constant current and constant field electronic thermal conductivity and the Wedemann-Franz law, which is widely used to extract lattice thermal conductivity from the experimentally measured total thermal conductivity.[8] *Work partially supported by ONR MURI grant. +Work done in collaboration with Daniel Bilc, Khang Hoang, Salameh Ahmad, and M. G. Kanatzidis and his group. 1. K. F. Hsu et. al. , Science 303, 818 (2004) 2. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993). 3. G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. U.S.A 93, 7436 (1996). 4. Khang Hoang, K. Desai, and S. D. Mahanti, Phys. Rev. B 72, 064102 (2005). 5. H. Hazama et al., Phys. Rev. B 73, 115108 (2006); Khang Hoang, S. D. Mahanti, and P. Jena (submitted to Phys. Rev. B). 6. D. Bilc et al. Phys. Rev. Lett. 93, 146403 (2004). 7. Khang Hoang et al. (submitted to Phys. Rev. Letters). 8. D. Bilc et al., Phys. Rev. B 74, 125202 (2006); S. Ahmad and S. D/ Mahanti (Unpublished)

11:00 AM U4.7

Galvanomagnetic Measurements of Neodymium Doped Lead Telluride. Vladimir Jovovic[1] and Joseph P. Heremans[2]; [1]Mechanical Engineering, The Ohio State University, Columbus, Ohio; [2]Mechanical Engineering and Physics, The Ohio State University, Columbus, Ohio.

A systematic study of the thermoelectric properties of alloys of PbSe with rare earth elements (Ce, Pr, Nd, Eu, Gd and Yb)[1] has shown an increase in thermopower perhaps due to a hybridization of 4f levels with the PbSe bands. As predicted by Mohan and Sofo[2] theory these high-density-of-state levels, if at Fermi level, can result in significant improvement in thermoelectric properties. We have found that largest improvement in thermopower is observed in PbSeNd alloys where we measured doubling of thermopower at high carrier concentrations as compared to PbSe. Here we study telluride alloys: we analyze set of $Pb_{1-x}Sn_xTe$:Nd with Nd concentrations up to 10% and x ranging from 0 to 1. Since Nd3+ is a donor in PbTe, we use counterdoping in two systems. The first system is PbTe + Nd_2Te_3 , which is electrically neural; the second system is the $Pb_{1-x}Sn_xTe$ + NdTe,

where the $Pb_{1-x}Sn_xTe$ alloys are naturally heaviliy *p*-type. Galvanomagnetic measurements are performed in standard flow cryostat at temperatures ranging from 80 to 600K and in magnetic field from -2.5 to 2.5 T. Measurements of electrical resistivity, thermopower, Hall and transverse Nernst-Ettinghausen effect are used to deduce the fundamental properties: the carrier density, mobility, effective mass and scattering exponent. Results are analyzed to evaluate the possible hybridization of Nd levels in the $Pb_{1-x}Sn_xTe$ bands. [1] V. Jovovic, S. Joottu Thiagarajan, J. West, J. P. Heremans, T. Story, Z. Golacki, W. Paszkowicz and V. Osinniy, submitted to Journal of Applied Physics (2007) [2] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. USA 93 7436 (1996)

11:15 AM U4.8
Optimization of High Thermoelectric Figure of Merit in p-type Ag1-x(Pb1-ySny)mSb1-zTem+2. Kyunghan Ahn and Mercouri G Kanatzidis; Chemistry, Northwestern University, Evanston, Illinois.

Thermoelectric (TE) power generation is the focus of considerable attention because of the potential for environmentally benign and cost-effective conversion of waste heat to electricity. The search for high TE efficiency materials is a quest to maximize the dimensionless figure of merit ZT = (σS2/κ)T, where σ is electrical conductivity, S is the TE power (Seebeck coefficient), and κ is thermal conductivity. Certain compositions of Ag(Pb1-ySny)mSbTe2+m (LASTT) series have been recently found to exhibit high performance p-type TE properties (ZT ~ 1.45 at 630 K). Varying the m and y values as well as the concentrations of Ag and Sb allows for control over carrier concentration, TE power, and thermal conductivity. We will present detailed investigations on the TE properties of p-type Ag1-x(Pb1-ySny)mSb1-zTem+2 (LASTT) series by tuning primarily through controlling m value and Pb/Sn ratio (y value) and secondarily the Ag and Sb concentrations (x and z values) because the LASTT system has not been optimized yet well. In addition we will present experimental evidence of the nanostructured nature of these materials which results in very low lattice thermal conductivity.

11:30 AM U4.9
High-Temperature Thermoelectric Properties of $Pb_{1-x}Sn_xTe$:In. Suraj Joottu Thiagarajan[1], Vladimir Jovovic[1], Joseph West[1], Joseph Heremans[1], T. Komissarova[2], Dmitriy Khokhlov[2] and A. Nicorici[3]; [1]The Ohio State University, Columbus, Ohio; [2]Moscow State University, Moscow, Russian Federation; [3]Institute of Applied Physics, Moldova Academy of Sciences, Kishinev, Moldova.

Indium in $Pb_{1-x}Sn_xTe$ alloys forms a narrow energy level which might hybridize with valence or conduction bands[a]. In this study we investigate interactions between Indium impurity levels and band at extended range of temperatures from 80 to 400K. In contrast to our previous work at 80 K [b], it turns out that the PbTe band structure is very temperature-dependent, and so is the location of the In level with respect to the conduction and valence band edge. Transport properties, measurements of electrical resistivity, thermopower, Hall and transverse Nernst-Ettingshausen effect are used to assess effective mass, and carrier mobility, Fermi energy level and scattering coefficient. Measurements are performed on a set of p and n type $Pb_{1-x}Sn_xTe$ indium doped alloys with Sn concentrations from 0 to 30% and In up to 3%. Using these measurements we evaluate the In level location in the bands at higher temperature. Hybridization at the Fermi levels can have positive effects on the thermoelectric properties of materials resulting from an increase in thermopower due to an increase in electron scattering exponent as predicted by Ravich, Nemov and Kaidanov. Our study evaluates possibility of increasing thermoelectric figure of merit of $Pb_{1-x}Sn_xTe$:In alloys at operating temperatures. [a] K. Hoang et al., APS Meeting Abstracts, 40012 (2007) [b] V. Jovovic et al., Electronic Materials Conference, Notre Dame, June 20-22, 2007 [c] V.I. Kaidanov et al., Sov. Phys. Semicond. 26, 113 (1992)

11:45 AM U4.10
N-type Lead-Chalcogenide Thermoelectric Materials Alloyed with Tin. Jan Dieter Koenig, Alexandre Jacquot and Harald Boettner; Thermoelectric Systems, Fraunhofer IPM, Freiburg, Baden-WÃƒÂ¼rttemberg, Germany.

IV-VI materials, especially lead-chalcogenides are used until now for mid-temperature thermoelectric applications. Currently PbTe doped with PbI2 is used as n-type material and TAGS85 or (Pb,Sn)Te with a tin content above x=0.25 as p-type legs. To increase the thermoelectric efficiency it is worth to look for an alternative n-type material. This alternative material should be preferentially also be based on lead-tin chalcogenides. Therefore we studied the preparation and thermoelectrical properties of n-type alloys respectively as thin film and as bulk materials. To do this, single crystalline thin film samples and also bulk single crystals of (Pb,Sn)Te and (Pb,Sn)Se in the composition range of a tin content below x=0.25 were grown by molecular beam epitaxie and by the unseeded vapour growth technique respectively. Recent temperature dependent measurements of the thermoelectric transport properties of a series of n-type (Pb,Sn)Te and (Pb,Sn)Se are presented. The alloying with tin results in a multifunctional effect: With increasing tin content the band gap reduces towards ideal values for applications in the room- and mid-temperature range. The effects of the tin alloying on the overall power factor and figure-of-merit (ZT) will also be discussed. It was found, that the stable or increasing carrier mobility and the reduction of the lattice thermal conductivity due to alloy scattering is the main reason for the ZT enhancement with increasing tin content. Based on these investigations the currently used n-type material could be substituted by the material systems presented in this paper.

SESSION U5: Bulk Thermoelectrics I
Chairs: David Singh and Jihui Yang
Tuesday Afternoon, November 27, 2007
Room 311 (Hynes)

1:30 PM *U5.1
Bulk Materials Research for Thermoelectric Power Generation Applications. George Nolas, Joshua Martin, Matthew Beekman and Xiumu Lin; Physics, University of South Florida, Tampa, Florida.

There are a variety of material systems employing different strategies in an effort to establish a new paradigm for thermoelectric materials performance. One approach is the PGEC, or "phonon-glass electron crystal", approach were research towards optimization of the electrical properties of very low thermal conductivity materials is key. Other efforts focus on materials that exhibit high power factors via quantum-confinement or nano-scale affects. Still others focus on "engineering" metastable phases that possess properties that are distinct, if not unique, to solid-state chemistry. All these approaches are valid and provide a fundamental knowledge base whereby present and future scientific materials discoveries will

lead to new technological improvements. This talk will focus on bulk materials, in particular those material systems currently under investigation in our laboratory and the requirements and strategies for their optimization towards improved thermoelectric properties.

2:00 PM U5.2

Thermoelectric Properties of Silicon and Germanium Network Polyhedra viewed from Physical Parameters. Katsumi Tanigaki[1], Takeshi Rachi[1], Jun Tang[1], Ryotaro Kumashiro[1], Shoji Yamanaka[2], Macros A Avila[2] and Toshiro Takabatake[2]; [1]Physics, Tohoku University, Sendai, Japan; [2]Hiroshima University, Hiroshima, Japan.

When the special conditions are constrained to the network formation in IVth group of elements like silicon, germanium and tin, nano materials having network polyhedra are produced. Although the sp3-hybridized bonding is favored in silicon and germanium different from carbon where both sp2- and sp3- hybridization are realized in graphite and diamond, a new series of materials featured by the polyhedral cage frameworks with sp2-characters have been sought in these days and lots of such materials, so called clathrates, have been synthesized. In these nano materials, one of the important issues is phonons. Because of the cluster cages and their large inner spaces inside, the phonons different from the conventional lattice phonons should be taken into account. For instance, intra-cluster phonons are believed to play an important role for giving rise to unique electronic states through electron-phonon coupling and endohedral atomic phonons with showing time- and space-dependent anharmonic oscillations are also expected to provide exotic interactions with conduction electrons at the Fermi surfaces. The latter phonons have recently been drawing much attention in materials science and are called as rattling phonons. The rattling phonons have freedom in motion and will break the symmetry of crystals. In this sense, phonons are glass-like and the electrons spreading over the polyhedral networks are crystal-like in silicon and germanium clathrates. This intriguing concept of phonon-glass and electron-crystal (PGEC) shows lots of possibilities of creating novel materials like good thermoelectric compounds. Among the compounds showing such features as regulated nano spaces that make it possible to accommodate atomic elements, like clathrates, skutterdites, pyrochlores and fullerides, clathrates will be one of the most perspective candidates to be applied to thermopower materials with high conversion figure of merits. In this meeting, we would like to present our recent systematic experimental studies on type I silicon and germanium clathrates [1-3] with emphasis on the three component type I clathrates (Sr,Ba)8(Ga,Al,In)16(Si,Ge)30. Depending on the component ratios, carrier type can be controlled between p and n for single crystals in this system and some of them show high performances as thermoelectric power materials. We will provide all sets of experimental parameters and discuss their electronic states on a basis of the information. The work is supported by Grand-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan as well as by the 21st Century Tohoku University COE program and the Center for Interdisciplinary Research Project in Tohoku University. [1] K. Tanigaki, et al, Nature Materials, 2, 653 (2004).[2] T. Rachi, K. Tanigaki et al., Phys. Rev. B, 72, 144504 (2005). [3] Takeshi Rachi , Katsumi Tanigaki et al., J. Physics and Chemistry of Solids 67, 1334-1337 (2006).

2:15 PM U5.3

Thermoelectric Properties of Silicon and Germanium Type III Clathrates $Ba_{24}IV_{100}$ (IV=Si and Ge). Takeshi Rachi[1], Harukazu Yoshino[2], Ryotaro Kumashiro[1], Hiroshi Fukuoka[3], Shoji Yamanaka[3], Keizo Murata[2] and Katsumi Tanigaki[1]; [1]Physics, Tohoku University, Sendai, Japan; [2]Physics, Osaka City University, Osaka, Japan; [3]Applied Chemistry, Hiroshima University, Higashi-Hiroshima, Japan.

Thermoelectric materials have been drawing lots of attentions for achieving high energy conversion from heat to electricity. To realize ideal thermoelectric power materials, many guiding principles have been applied for various materials, such as degenerate semiconductors, strongly correlated electron system, magnetic spin system and quasi-crystals. Differently from these approaches, the concept of Phonon-Glass-Electron-Crystal (PGEC) has recently been introduced. Among the materials showing such possibilities, clathrates are considered to be one of the best compounds and experimental tests have been made mainly for type I clathrates. Since clathrates have a variety of structural types, it would be very intriguing to have similar tests for other types of clathrates. In this meeting, we would like to present our recent results on the thermoelectric power measurements for silicon and germanium type III clathrates, $Ba_{24}IV_{100}$ (IV=Si and Ge). $Ba_{24}Si_{100}$ can only be synthesized under high pressure, while $Ba_{24}Ge_{100}$ can be prepared under ambient pressure. The thermoelectric powers for the both compounds have been measured using a home-made apparatus and an accessory cell attached to PPMS (Quantum Design). The Seebeck coefficient of $Ba_{24}Si_{100}$ shows a linear dependence as a function of temperature (T) from 300 K down to 100K, but the temperature evolution dramatically changed in low temperature region. On the other hand, a T-linear dependence can be observed in a narrow window of 300 K to 230 K in the case of $Ba_{24}Ge_{100}$. The noticeable change observed around 200 K in $Ba_{24}Ge_{100}$ was reported in the previous studies and are suggested to be related to the small local Jahn Teller distortion caused by the motion of the endohedral Ba atoms. When the Seebeck coefficients are compared between $Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$ at 300 K, the former shows the value of -6.6 μVK^{-1} and the one for the latter is -18 μVK^{-1}. We will discuss figure of merits of both systems using the other physical parameters. Considering the larger accommodating inner space created in the germanium polyhedral framework than that in the silicon one, the comparison will also be made between type I and type III from the view point of figure of merits.

2:30 PM U5.4

High Temperature Thermoelectric Efficiency in $Ba_8Ga_{16}Ge_{30}$. Eric S Toberer[1], Mogens Christensen[2], Bo Brummerstedt Iversen[2] and Jeffrey Snyder[1]; [1]Materials Science, California Institute of Technology, Pasadena, California; [2]Department of Chemistry, University of Aarhus, Langelandsgade, Denmark.

The identification of the clathrate $Sr_8Ga_{16}Ge_{30}$ as a potential high-zT thermoelectric material greatly increased the interest in the transport properties of this class of compounds. This early work estimated a maximum zT in excess of 1.0 above 700K. These initial predictions largely proved true, with the clathrate $Ba_8Ga_{16}Ge_{30}$ showing excellent high temperature performance and stability. In comparison to the state-of-the-art material, SiGe, the thermoelectric figure of merit (zT) is equivalent (zT ~ 1 at 1000K) and the segmentation compatibility with lower temperature materials is significantly better. Here, we have formed polycrystalline materials and grown a large single crystal of $Ba_8Ga_{16}Ge_{30}$ using the Czochralski method.

Measurement of the thermal expansion, electrical conductivity, thermal conductivity and Seebeck coefficient to 1173 K permit a calculation of zT (max zT of 0.8) and compatibility factor. The polycrystalline and single crystalline materials show identical values of zT, suggesting polycrystalline materials may be practical for applications. Further optimization of the thermoelectric efficiency requires precise tuning of the Ga:Ge ratio and is underway. Modeling of segmented thermoelectrics based on $Ba_8Ga_{16}Ge_{30}$ indicates a much higher level of compatibility with Bi_2Te_3/PbTe than

SiGe, permitting a leg efficiency of 16.4% from 300-1123K.

2:45 PM U5.5

Synthesis and Characterization of Inorganic Clathrate-II Materials. Matt Beekman and George S. Nolas; Department of Physics, University of South Florida, Tampa, Florida.

Inorganic clathrate materials are characterized by a covalently bonded framework, typically of Si, Ge, or Sn, which can encapsulate guest species inside polyhedral cages formed by the framework. Compounds with the clathrate-I crystal structure have been extensively investigated, and continue to generate much interest due to their promising thermoelectric properties. Phases with the clathrate-II crystal structure, however, still remain to be well characterized. Inorganic clathrate-II materials offer the unique ability to vary the guest concentration, which has significant implications for the control of their electrical and thermal transport properties. We present here recent results on the synthesis and characterization of silicon and germanium clathrate-II materials. The transport properties of Na_xSi_{136} clathrates show strong dependence upon the guest content *x*, indicating a potential route for transport property "tuning." We present results from an investigation into the possible "phase space" of inorganic clathrate-II phases, an exploration of new clathrate-II compositions including framework substitution by elements of Group III, as well as transition metals in clathrate-II compounds. The potential inorganic clathrate-II materials hold for thermoelectric applications will be discussed.

3:30 PM U5.6

Thermoelectric Properties of $In_xCo_{4-y}Ni_ySb_{12}$ Skutterudite Compounds. Veronique Da Ros[1], Juliusz Leszczynski[1], Bertrand Lenoir[1], Anne Dauscher[1], Christophe Candolfi[1], Philippe Masschelein[1], Christine Bellouard[2], Christian Stiewe[3], Eckard Müller[3] and Jiri Hejtmanek[4]; [1]Laboratoire de Physique des Materiaux, Ecole Nationale Superieure des Mines de Nancy, Nancy, France; [2]Laboratoire de Physique des Matériaux, Université Henri Poincaré, Nancy, France; [3]Institute of Materials Research, German Aerospace Center DLR e.V, Köln, Germany; [4]Institute of Physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic.

The preparation of partially filled n-type $In_xCo_4Sb_{12}$ skutterudite compounds has been recently reported. The results were particularly promising, the materials exhibiting a ZT value far higher than one at moderated temperature. An even higher value has been achieved by modulating the void filling by two different elements (In and Ce). In this paper, we propose to investigate another way to tune the electrical and thermal properties by substituting Co atoms by Ni atoms in $In_xCo_4Sb_{12}$. $In_xCo_{4-y}Ni_ySb_{12}$ polycrystalline samples have been prepared by a conventional metallurgical route. Structural analyses have been carried out by X-ray diffraction. The chemical composition and micro-homogeneity have been checked by electron probe microanalysis. Measurements of the electrical resistivity, thermoelectric power, thermal conductivity and Hall coefficient have been performed between 4 and 800 K. The influence of the presence of Ni on the thermoelectric properties of $In_xCo_4Sb_{12}$ compounds will be presented and discussed.

3:45 PM U5.7

Dual-Frequency Resonant Phonon Scattering in BaxRyCo4Sb12 (R = La, Ce, and Sr). Jihui Yang[1], Wenqing Zhang[2], Shengqiang Bai[2], Zhigang Mei[2] and Lidong Chen[2]; [1]R&D Center, General Motors Corp., Warren, Michigan; [2]State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

Low temperature transport properties of polycrystalline dual-element-filled skutterudites BaxRyCo4Sb12 (R=La, Ce, and Sr) are reported. Remarkably the combination of Ba and La, or Ba and Ce is much more effective in reducing lattice thermal conductivity than Ba and Sr, in spite of the much higher total void filling fraction in BaxSryCo4Sb12. Our density functional theory calculations and experimental data suggest that multiple-filled skutterudites using filler elements of different chemical nature, such as the rare-earths, the alkaline-earths, or the alkalines provide a broader range of resonant phonon scattering. The thermoelectric figure of merit of filled skutterudites can likely be improved by means of such multiple-element void filling.

4:00 PM U5.8

Ternary Skutterudites: Anion Ordering and Thermoelectric Properties. Paz Vaqueiro and Gerard G. Sobany; Heriot-Watt University, Edinburgh, United Kingdom.

Materials with the skutterudite structure, MX3 (M = Co, Rh or Ir and X = P, As or Sb) possess attractive thermal and electrical transport properties for thermoelectric applications at temperatures over the range 650-900K. While binary skutterudites, MX3, have been widely investigated, little is known about the related ternary skutterudites, which can be prepared by isoelectronic substitution at the anion or cation sites. Our recent research efforts have been centered on the synthesis and characterisation of ternary skutterudites obtained by substitution at the anion site, X, by a pair of elements from groups 14 and 16. The skutterudite-related materials AB1.5Q1.5 (A = Co, Rh, Ir, B =Ge, Sn, Q = S, Te) have been synthesized and structurally characterised by high-resolution X-ray and neutron powder diffraction. Diffraction data are consistent with the presence of anion ordering, which results in a lowering of the symmetry from cubic to rhombohedral. Measurements of the resistivity, Seebeck coefficient and thermal conductivity have been carried out. The electrical transport properties of these materials are consistent with semiconducting behaviour, and large values of the Seebeck coefficient have been observed for several of these phases. In addition, these materials exhibit significantly lower thermal conductivities than their binary counterparts.

4:15 PM U5.9

Enhanced Thermoelectric Figure of Merit in $Ba_xYb_yCo_4Sb_{12}$ Skutterudites. Ctirad Uher, Xun Shi and Huijun Kong; Physics, University of Michigan, Ann Arbor, Michigan.

Skutterudites are among a handful of novel materials that are being intensely pursued in hope of developing more efficient thermoelectrics for power generation applications at temperatures between 500K - 850K. Filling the voids in the skutterudite structure by different fillers is an effective way of reducing thermal conductivity because a broader range of phonons is scattered. This approach is particularly effective when fillers with different

phonon contrast (different masses and resonant frequencies) are used. We prepared double-filled skutterudites ($Ba_xYb_yCo_4Sb_{12}$)using a melting method and studied their high temperature thermoelectric properties from 300K to 800K. The double-filled materials show a very low lattice thermal conductivity yet maintain good electrical transport properties. The highest ZT achieved in $Ba_xYb_yCo_4Sb_{12}$ is 1.36 at 800K.

4:30 PM U5.10

Complex Zintl Phases for Thermoelectric Power Generation. Jeff Snyder, California Institute of Technology, Pasadena, California.

Complex Zintl phases and polar intermetallics make ideal candidates for thermoelectric materials because the necessary "electron-crystal, phonon-glass" properties can be engineered with an understanding of the Zintl chemistry [1]. Zn4Sb3 achieves high thermoelectric figure of merit by having extraordinarily low lattice thermal conductivity that can be attributed to the presence of disorderd interstitial zinc atoms and nanometer sized domains. The Clathrate Zintl Phase Ba6Ga16Ge30 has low thermal lattice thermal conductivity due to the complex cage-host structure and high thermoelectric efficiency due to the good compatibility with Pbte. A recent example is the discovery that Yb14MnSb11, a transition metal Zintl compound, has twice the zT as the SiGe based material currently in use at NASA. This talk will outline a strategy to discover new high zT materials in Zintl phases, and presents results pointing towards the success of this approach. 1. Susan M. Kauzlarich, Shawna R. Brown and G. Jeffrey Snyder "Zintl phases for thermoelectric devices" Dalton Trans. p. 2099 (2007).

4:45 PM U5.11

Synthesis and Thermoelectric Properties of M3Ni3Sb4 (M=Zr or Hf). James Robert Salvador[1], Jihui Yang[1] and Hsin Wang[2]; [1]R&D and Planning, General Motors, Warren, Michigan; [2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The Seebeck coefficient, electrical resistivity, thermal conductivity and Hall-effect for the cubic "Zintl" phases M3Ni3Sb4 (M= Zr or Hf) were measured. These materials were synthesized by induction melting of the elements. Powder X-ray diffraction and electron probe microanalysis reveal that a single phase of the Y3Au3Sb4 structure type was obtained. The Y3Au3Sb4 structure is a stuffed variant of the Th3P4 structure and the compounds presented are isostructural to Ce3Pt3Bi4, a known Kondo insulator and RE3Au3Sb4(RE = Gd, Nd, Ho, and Sm) which have been shown to posses good thermoelectric properties. Ab initio calculations demonstrate that a hybrization gap is present in M3Ni3Sb4 (M= Zr or Hf) in an analogous manner to the half-Huesler compound ZrNiSn, and may lead to interesting transport properties in these systems. The Seebeck coefficient of the Zr analog was found to change sign from negative to positive at 150 K and return to a negative value above 650 K; while Hf3Ni3Sb4 showed similar behavior becoming positive at 140 K. Hf3Ni3Sb4 with significant Sb vacancies was found to have a positive Seebeck coefficient above 2 K attaining a maximum value of 0.202 mV/K at 560 K. Hall measurements were performed to investigate this phenomenon. Both compounds exhibit low thermal conductivity with values of 4.35 W/m-K and 2.66 W/m-K at room temperature for The Zr and Hf analogs respectively. The low thermal conductivities and large Seebeck coefficients make these materials interesting for intermediate to high temperature thermoelectric applications. The effects of Sn doping and Co alloying were also explored. This work was supported by GM and by DOE under corporate agreement DE-FC26-04NT42278

SESSION U6: Poster Session
Tuesday Evening, November 27, 2007
8:00 PM
Exhibition Hall D (Hynes)

U6.1

Zintl Phase as Thermoelectric Materials: Synthesis, Structure and Properties of $Yb_5Al_2Sb_6$. Iliya Todorov[1], Duck-Young Chung[1] and Mercouri Kanatzidis[2,1]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [2]Department of Chemistry, Northwestern University, Evanston, Illinois.

Zintl phases are an understudied class of compounds with respect to their potential as materials for high temperature thermoelectric applications. Many of the structural, bonding and physical characteristics of this class of compounds, such as fairly small band gaps and complex anionic frameworks stabilized by weakly bounded electropositive cations, are similar to those found in many of today's best thermoelectric materials. A recent successful example from this class of compounds is the transition metal Zintl phase $Yb_{14}MnSb_{11.8}$. This compound has demonstrated that its thermoelectric figure of merit ZT reaches 1.0 at 1223 K. These findings provide the first indication of a new field that could be full of new thermoelectric candidates. We present here the synthesis, crystal structure, spectroscopic properties, and electronic structure of a new member of the Zintl family, $Yb_5Al_2Sb_6$. The compound crystallizes in the $Ba_5Al_2Bi_6$ structure type and is isostructural and isoelectronic to the recently reported $Yb_5In_2Sb_6$. The preliminary measurements show the conductivity and Seebeck coefficient of 512 S/cm and 48 μV/K at 755 K, respectively. Investigations of solid solutions of this phase, doping effects and chemical modifications will be presented.

U6.2

The Effect of $Ca_3Co_2O_6$ Addition on the Thermoelectric Properties of Bulk $Ca_3Co_4O_9$. O-Jong Kwon, Sang-Hoon Lee, Sung-Hwan Bae, Sejin Yoon and Chan Park; Department of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

Recently, layered cobaltates have emerged as promising thermoelectric (TE) materials due to their excellent TE properties.[1] So far, many works have focused on thin-film layered cobaltates (mostly $Ca_3Co_4O_9$ (Ca349)) which have far better performance than bulk cobaltates. For the practical application, the fabrication of bulk layered cobaltates which have good thermoelectric property is needed. In this study, to investigate the effect of adding $Ca_3Co_2O_6$ (Ca326) to Ca349 on the thermal and electrical conductivities and thermoelectric properties, polycrystalline mixture of Ca349 and a small amount of Ca326 was prepared in air at 900°C using solid state reaction method from high purity $CaCO_3$ and Co_2O_3 powder. The amount of Ca326 added to Ca349 was from 0 to 10 mol%. In order to distinguish the effect of Ca326 addition from that of microstructure, samples with almost identical grain sizes and densities were prepared. The microstructures of samples were observed using FE-SEM. Electrical conductivity, Seebeck coefficient and figure of merit were measured by Harman's method. Thermal conductivity was calculated from other quantities measured. The effect

of addition of Ca326 to Ca349 on the thermoelectric properties of the mixture will be presented. The evolution of the microstructure when Ca326 is added to Ca349, and the way the microstructure can be controlled, will also be discussed.

[1] Y. F. Hu, et al, Appl. Phys. Lett. 87, 171912(2005).

U6.3

Preparation and Properties of Srn+1TinO3n+1 Ruddlesden-Popper Homologous Series by Metal-citric Acid Complex Decomposition Method. Keishi Nishio[1], Kazuhiko Hukuda[1], Hirohumi Takenouchi[1], Hideo Mae[4], Masakatsu Fujimoto[4], Tomohiro Imai[2], Noriaki Hamada[2], Tsutomu Iida[1], Tohru Kineri[5] and Tsuneo Watanabe[3]; [1]Department of Materials Science and Technology, Tokyo University of Science, Noda-shi, Chiba, Japan; [2]Department of Physics, Tokyo University of Science, Noda-shi, Chiba, Japan; [3]Department of Applied Electronics, Tokyo University of Science, Noda-shi, Chiba, Japan; [4]Yamaguchi Prefectural Industrial Technology Institute, Ube-shi, Yamaguchi, Japan; [5]Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda-shi, Yamaguchi, Japan.

Oxide thermoelectric materials are thermal stability and harmless in comparison with intermetallic compounds such as Bi2Te3. Furthermore, since a metal oxide is better in terms of ease of preparation and control of chemical composition, strontium titanium oxide is well suited for the material. Although SrTiO3 is an insulator, it can be doped with impurities to become a semiconductor with high electronic conductivity and thermal electromotive force. There have been a few research reports about the preparation and properties of SrTiO3 for its application to thermoelectric power generation systems. In this study, the Srn+1TinO3n+1 Ruddlesden-Popper homologous series was investigated. This material exhibits a wide range of electric behaviors, from a high-dielectric-constant tunable-paraelectric in its undoped form to a metallic superconductor when it is doped with a variety of elements. The Srn+1TinO3n+1 and a yttrium-doped Srn+1TinO3n+1 Ruddlesden-Popper homologous series were prepared by thermal decomposition of metal citric acid complex. The starting solution consisted of strontium acetate and titanium alkoxide as the raw materials. Citric acid was used as the chelating agent, and ethanol and distilled water were mixed as a solvent. Single phase Sr2TiO4 and Sr3Ti2O7 were produced without SrCO3 by heat-treatment at above 1073 and 1473 K, respectfully, for 3 hours. Single phase Sr4Ti3O10 could not be produced. The samples consisted of Sr4Ti3O10 and SrTiO3 phases. Observation by scanning electron microscopy showed that the grain shape of the Sr2TiO4 was plate-like, while those of the Sr3Ti2O7 and Sr4Ti3O10 were not and the grains had large numbers of pores. High-density Sr2-xYxTiO4 (x=0 to 0.06) ceramic samples were produced under hot-press conditions (1823 K for 1 hour at a uniaxial pressure of 31.2 MPa). Although the undoped samples were insulators, the yttrium-doped samples showed high electrical conductivity (i.e. that of Sr1.98Y0.02TiO4 was ρ=8.5×10-5 Ωcm). The Seebeck coefficient of Sr1.98Y0.02TiO4 was −160.7 μV/K, and the thermal conductivity was 3.38 W/mK.

U6.4

Design and Evaluation of n-type Si_1-x_Ge_x_ as a Thermoelectric-conversion Material. Tomohiro Imai[1], Tsutomu Iida[2], Yuki Miyata[2], Takashi Itoh[2], Hiroki Funashima[1], Yoshifumi Takanashi[2] and Noriaki Hamada[1]; [1]Department of Physics, Tokyo University of Science, Chiba Noda-shi, Yamazaki 2641, Japan; [2]Department of Materials Science and Technology, Tokyo University of Science, Chiba Noda-shi, Yamazaki 2641, Japan.

Alloys of silicon and germanium (Si_1-x_Ge_x_) are ecologically friendly semiconductors and important materials, not only for microelectronic devices, but also for solid-state power generators such as solar cells and thermoelectric devices. This is mainly due to their chemical stability, mechanical strength at elevated temperatures, and a close match of the n-/p-type alloys which enables better device operation. For thermal-to-electric energy-conversion, Si_1-x_Ge_x_ with x~0.3 to 0.8 can minimize the thermal conductivity due to the random ordering of the constituent atoms in the crystal. Since Si_1-x_Ge_x_ exhibits a random-alloy system, a systematic calculation, which can predict thermoelectric properties such as Seebeck coefficient and thermal conductivity, for various compositions, x, has not been adequately performed. We have evaluated the thermoelectric-conversion materials of the type Si_1-x_Ge_x_ on the basis of first principles calculations, and have designed new materials from the viewpoint of Computational Materials Design (CMD). The first-principles calculations were carried out by using All-electron Band-structure CAlculation Package (ABCAP), in which the full-potential linearized augmented-plane-wave (FLAPW) method is employed with the local density approximation (LDA). The thermoelectric power has been evaluated on the basis of the Bloch-Boltzmann theory. Although Si_1-x_Ge_x_ constitutes a random-alloy system, it is treated using the super-cell method in the band-structure calculations, where atoms of Si and Ge are arranged in a large unit cell. The valence band and, therefore, the Seebeck coefficient hardly change with Ge concentration for the p-type system. The valleys in the conduction band can be modified by varying the Ge composition, x. We have found an optimum carrier-concentration to achieve a large thermoelectric power for the n-type Si_1-x_Ge_x_ system. For the x values in Si_1-x_Ge_x_ , predicted from the ABCAP calculation, a melt growth was performed using a die-casting growth technique, with subsequent sintering. Since the Si-Ge system exhibits a complete series of solid solutions with a phase relationship, it is not easy to precipitate crystals when selectively possessing a certain composition of silicon or germanium using conventional growth methods. To conduct a bulk crystal growth of Si_1-x_Ge_x_, we applied the die-casting growth technique, combined with an advanced version of the Bridgman method, which provides Si_1-x_Ge_x_ precipitation in a form completely different from that predicted by the Si-Ge phase diagram. Using the powder from grown crystals, samples were prepared by the plasma activated sintering (PAS) method. For the sintered samples, thermoelectric properties, such as Seebeck coefficient, electrical conductivity, and thermal conductivity, were measured over a temperature range from room temperature to 873 K. We also present the results of the calculated dimensionless figure of merit, ZT.

U6.5

High Energy Ball Mill Synthesis and Thermoelectric Properties of the Yb(14-x)CaxMnSb(11-y)Biy System. Kurt Star[1], Teruyuki Ikeda[2], Chen-Kuo Huang[3], Bruce Dunn[1] and Jean-Pierre Fleurial[3]; [1]Department of Material Science and Engineering, University of California Los Angeles, Los Angeles, California; [2]Material Science Department, California Institute of Technology, Pasadena, California; [3]Power and Sensor Systems Group, Jet Propulsion Laboratory/California Institute of Technology, Pasadena, California.

Yb14MnSb11 is a very promising thermoelectric material for high temperature applications. This compound is a member of a large family of Zintl phases with a "14-1-11" A14MPn11 stoichiometry (Pn = P, As, Sb, Bi; A = Ca, Ba, Sr, Yb, Eu; Mn = Mn, Al, Cd, Ga, In, Zn). Yb14MnSb11 exhibits low lattice thermal conductivity values and a p-type semimetallic behavior with values of the non-dimensional figure of merit ZT peaking at 1.4 above 1200 K. There is a significant interest in investigating how substitutions on any of the atomic sites impact the charge carrier concentration, band gap and lattice thermal conductivity. High energy ball milling has been shown to be a convenient method of synthesis to prepare Yb14MnSb11 and it has been used here to explore the various solid solution systems derived from this compound. High energy ball milling is a non-equilibrium process and

not all of the 14-1-11 compounds are easily formed with this method. Experimental work on several compositions has demonstrated that high energy ball milling works best in 14-1-11 systems which also have a stable A11Pn10 phase present. The Yb(14-x)CaxMnSb(11-y)Biy solid solutions have been selected for their potential for significant reductions in lattice thermal conductivity values while maintaining good electrical properties at lower temperatures than the pure Yb14MnSb11. Characterization of the synthesized compositions was done by X-Ray diffraction, electron microprobe, and high temperature measurements of the electrical and thermal transport properties up to 1275 K. The experimental results are compared to that of Yb14MnSb11 samples prepared by the same high energy ball milling technique

U6.6

Grain Boundary Structure in Bismuth Telluride-Based Thermoelectric Alloys. Douglas L. Medlin, N. Y. C. Yang and J. M. Chames; Sandia National Laboratories, Livermore, California.

In this presentation we report our observations of the structure of grain boundaries in bismuth telluride-based thermoelectric materials. We have investigated the macroscopic crystallography and atomic-scale structure of grain boundaries and related crystallographic defects in device-grade alloys of composition $(Bi_{0.2}Sb_{0.8})_2Te_3$ and $Bi_2(Se_{0.1}Te_{0.9})_3$ using electron backscattered diffraction (EBSD) and high resolution transmission electron microscopy (HRTEM). In many cases, we find grains that are sub-divided by twin boundaries. These interfaces are faceted on (0001) planes and separate regions of crystal that are related by a 180° rotation about the crystallographic c-axis. The crystal structure of bismuth telluride can be described as a stacking of 5-layer units, or "quintets", of alternating Te and Bi layers along the c-axis (i.e. in a sequence: ...-Te-Bi-Te-Bi-Te-). A double layer of Te atoms arises every five planes where these units are joined. (In the ternary alloys, Sb substitutes for Bi and Se substitutes for Te). A basic question is how this stacking is related to the interface structure. Our calculations of the contrast produced in HRTEM images of these materials show that the position of the double Te layer can be easily distinguished by its significantly brighter lattice fringe intensity. This feature provides a useful metric for interpreting the defect structure. For instance, our observations suggest that the position of the interface in the basal twin boundary lies within the 5-layer stacking unit rather than between the double Te layers, a result that is contrary to what might have been expected given the weaker interlayer bonding across the double Te layers. We will discuss the relationship of the basal twin to the structure of more general boundaries in the bismuth telluride class of alloys. In particular, establishing the nature of the basal plane termination is important in cases where strong crystallographic texture provides grain orientations that are conducive to interfacial faceting parallel to this plane. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States DOE-NNSA under contract DE-AC04-94AL85000. The authors acknowledge Dr. J. Sharp, Marlow Industries, for providing the alloys investigated in this study.*

U6.7

Thermoelectric Properties of Phase Separated Composite of Ln-Doped SrTiO3 and TiO2 Micro Crystals. Kiyoshi Fuda[1], Kenji Murakami[1] and Shigeaki Sugigiyama[2]; [1]Akita University, Akita City, Japan; [2]Akita pref. Ind. Tech. Center, Akita City, Japan.

It seems that no satisfactory TE property has been found in n-type oxide bulk materials even though Al-doped ZnO and La-doped SrTiO3 have high thermoelectric (TE) responses. Difficulty in developing high-performance TE materials seems to lie in finding low thermal conductivity in such oxides. The purpose of this study is to find a possibility to make an n-type TE oxide bulk material having low thermal conductivity and excellent TE properties as well. For this purpose, we fabricated and examined a series of composites constructed of TiO2 and Ln-doped SrTiO3 fine crystals. The composites were prepared via two processing steps: (1) precursor oxide preparation by wet processes; (2) sintering by using spark plasma sintering (SPS) apparatus. The microscopic structure was examined by using scanning electron microscope (SEM; HITACHI S-4500 model) attached with an energy dispersive x-ray spectroscopy. The electrical conductivities and the Seebeck coefficients were measured simultaneously using an ULVAC ZEM-1 instrument in helium atmosphere. The thermal diffusivities were measured by a laser flash method in vacuum. The composites obtained here were found to commonly have a mosaic type texture constructed of TiO2 and SrTiO3 fine particles with a typical size of 500 nm. The thermal conductivity values measured for three samples with different contents are ranged between 3 and 4 Wm-1K-1 in the temperature range from room temperature to 800 C. The values are apparently lower than the value for single crystal SrTiO3 samples presented in literature. Taking account the other TE data, e.g. Seebeck coefficient and electrical conductivity, we calculated dimensionless figure of merit, ZT, to be at maximum 0.15 at 800°C.

U6.8

Variation in the Einstein Temperature of Guest Atoms in Ba-Ge-X type-III Clathrate Compounds. Katsushi Tanaka, Jung-Hwan Kim, Kyosuke Kishida and Haruyuki Inui; Materials Science & Engineering, Kyoto University, Kyoto, Japan.

Clathrate compound is one of the candidate materials for thermo-electric power generation because it exhibits a high Seebeck coefficient, low electro resistivity and thermal conductivity. We have found that the Ba-Ge based type-III compounds exhibit a superior thermoelectric properties with the dimensionless figure of merit, ZT, larger than unity resulting from the decrease in carrier density and in lattice thermal conduction by alloying with a ternary element. The former is simply explained by applying the Zintl concept for estimation the carrier density. The latter is, however, not simply explained. We have performed a powder X-ray diffraction analysis with a synchrotron radiation and derived the variation in the Einstein temperature of guest atoms in Ba-Ge-X type-III clathrate compounds. The variation in the temperatures determined are explained not only by the size of cage framework but also by the atomic radius of the alloying element, indicating that a free space for guest atoms is important to lower the rattling frequency.

U6.9

The Effect of Bi Addition on Thermoelectric Properties of the Sintered Heusler Alloy Fe2VAl. Masashi Mikami[1], Keizo Kobayashi[1], Kiminori Hazumi[2] and Yoichi Nishino[2]; [1]National Institute of Advanced Industrial Science and Technology, Nagoya, Japan; [2]Nagoya Institute of Technology, Nagoya, Japan.

A Heusler alloy, Fe2VAl, is a promising candidate for thermoelectric power generation near room temperature because of its high thermoelectric power factor compared to a Bi-Te system. In the Fe2VAl system, the electrical conductivity and the Seebeck coefficient are enhanced simultaneously by the off-stoichiometry of Al content or the element partial substitution, such as Si or Ge for the Al site and Ti for the V site. The thermoelectric power factor reaches 5.9 × 10-3 W/mK2 at 300 K. In addition, because of its high mechanical strength and excellent resistance to oxidation and corrosion, a durable thermoelectric module can be fabricated using this alloy. The thermoelectric figure of merit of this alloy is poor, however, because of its high thermal conductivity: ca. 26 W/mK. The thermoelectric energy conversion efficiency is lower than that of state-of-the-art

thermoelectric materials. Reduction of thermal conductivity is therefore required for practical applications. In this study, we prepared a Fe2VAl0.9Si0.1/Bi composite using pulse-current sintering technique with fine powder prepared by mechanical alloying. The grain size of Fe2VAl0.9Si0.1 part was 200-300 nm. On the other hand, the grain size of Bi was reduced by increasing the mechanical alloying processing time and nanometer sized grains were obtained. The thermal conductivity decreased with the decrease in Bi grain size, while electrical resistivity slightly increased. Although Seebeck coefficient was reduced by a negative effect of Bi incorporation on the Fe2VAl0.9Si0.1 crystal structure, the introduction of Bi nanoinclusions in the sintered Heusler material was effective to reduce the thermal conductivity without degradation of electrical conductivity and consequently improved the thermoelectric figure of merit.

U6.10

Synthesis and High Temperature Thermoelectric Properties of Nano Bulk Silicon and Silicon-Germanium Semiconductors. Sabah Bux[1,2], Richard G. Blair[3], Chen-Kuo Huang[2], Pawan Gogna[2], Richard B. Kaner[1] and Jean-Pierre Fleurial[2]; [1]Chemistry and Biochemistry and California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California; [2]Power and Sensors Systems Group, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; [3]Chemistry, University of Central Florida, Orlando, Florida.

Previous work in the 1960s demonstrated the use of solid solutions as a way to reduce the lattice thermal conductivity using point defect phonon scattering which significantly increased ZT values. It has been theorized that much larger reductions could be achieved through boundary scattering by engineering materials with a very high density of interfaces. Current research is focused on achieving such effects in 3-dimensional bulk semiconductors through high pressure sintering of Si and $Si_{1-x}Ge_x$ nanoparticles. The unfunctionalized Si and $Si_{1-x}Ge_x$ nanoparticles were synthesized using the technique of high-energy ball milling and mechanical alloying from the elements. Doped and undoped samples were characterized by powder X-ray diffraction and transmission electron microscopy. Thermal conductivity measurements on the densified pellets show a drastic reduction in the lattice thermal conductivity by up to a factor of 30 at room temperature compared to that of single crystalline samples. However, charge carrier mobility values remained fairly high, and the combination of the low thermal conductivity and relatively high power factor leads to an unprecedented increase in the ZT of pure heavily doped "nano bulk" Si by almost a factor of 3.5 over single crystal Si. Kinetic studies for optimization of the synthesis of the nanoparticles via mechanical alloying as a function of thermal conductivity, Hall mobility, carrier concentration, resistivity, crystallite size and nanoparticle distribution are presented and discussed.

U6.11

Synthesis and Thermoelectric Properties of Y Doped SrTiO3 by Modified Pechini's Method. Hirohumi Takenouchi[1], Tomohiro Imai[2], Hideo Mae[5], Masakatsu Fujimoto[5], Tohru Kineri[4], Tsutomu Iida[1], Noriaki Hamada[2], Tsuneo Watanabe[3] and Keishi Nishio[1]; [1]Department of Materials Science and Technology, Tokyo University of Science, Noda-shi, Chiba, Japan; [2]Department of Physics, Tokyo University of Science, Noda-shi, Chiba, Japan; [3]Department of Applied Electronics, Tokyo University of Science, Noda-shi, Chiba, Japan; [4]Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, Sanyoonoda-shi, Yamaguchi, Japan; [5]Yamaguchi Prefectural Industrial Technology Institute, Ube-shi, Yamaguchi, Japan.

Oxide thermoelectric materials are thermal stability and harmless in comparison with intermetallic compounds such as Bi2Te3. Mainly, cobalt oxide compounds including NaxCoO2 and Ca3Co4O9 have high thermoelectric properties. But they are p-type thermoelectric materials. High-performance n-type oxide materials are desired for p-n junction of thermoelectric device. One of high-performance n-type thermoelectric materials is SrTiO3. However SrTiO3 is a dielectric material, oxygen-deficient SrTiO3, Nb-doped SrTiO3, La-doped SrTiO3 and Y-doped SrTiO3 have been found to show electrical conduction. Particularly, Y-doped SrTiO3 shows high electrical conductivity in contrast to the other trivalent cation doped SrTiO3. In addition, it is reported that Y-doping reduces the thermal conductivity. In this study, we tried to prepare Sr1-xYxTiO3 ceramics having highly thermoelectric properties. At the same time, thermoelectric properties (Sr1-xYxTiO3 x=0-0.10) were calculated by the virtual crystal method. The Sr1-xYxTiO3(x=0 to 0.06) precursor powder was prepared using a modified Pechini's method and the powder was sintered by hot press (HP) process. Precursor solution was prepared with metal salts (Sr(OCOCH3)2 and Y(OCOCH3)3), metal alcoxide (Ti[OCH(CH3)2]4), citric acid, ethanol, acetic acid and H2O. The precursor solution was heated at 823K for 5h after drying at 353K for 8h to obtain the precursor powder. It is confirmed that SrTiO3 single phase was obtained without residue organics or creation of SrCO3 by heat treatment above 823 K. In this method, pure SrTiO3 could be obtained by lower temperature compared with normal solid-state reaction method. To obtain the ceramics, the precursor powder was placed in a graphite die and heated to 1673 K and then kept at that temperature for 1h under a pressure of 31MPa. The obtained ceramics had high bulk densities larger than 99% of the theoretical density. Those samples of the Seebeck coefficient and electrical conductivity were measured by the standard four-probe method in flowing He gas atmosphere in the temperature range from 323 to 923 K. The conductivity of SrTiO3, Sr0.97Y0.03TiO3 and Sr0.94Y0.06TiO3 was 6.61×102, 5.61×103 and 1.58×104 S/m at room temperature, respectively. The Seebeck coefficient of SrTiO3, Sr0.97Y0.03TiO3 and Sr0.94Y0.06TiO3 was -548, -264 and -196μV/K at room temperature, respectively.

U6.12

Thermoelectric Properties of La-doped $BaSi_2$ and $(Ba,Sr)Si_2$ Solid Solutions. Kohsuke Hashimoto, Ken Kurosaki, Hiroaki Muta and Shinsuke Yamanaka; Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Japan.

Metal silicides have attracted attention as new thermoelectric materials because they are environmentally-friendly. For example, the thermoelectric properties of $FeSi_2$ and Mg_2Si have been widely studied, and an excellent thermoelectric figure of merit (ZT = 1.1) was achieved in the n-type Mg_2(Si,Sn) system [1]. In our previous study [2], it was found that $BaSi_2$ indicated quite low thermal conductivity, which is comparable to or less than those of typical thermoelectric materials such as Bi_2Te_3. However, $BaSi_2$ indicated very high electrical resistivity due to the low carrier concentration. Consequently, the dimensionless figure of merit (ZT) of $BaSi_2$ is not so high: 0.01 at 954 K. In the present study, we have tried to improve the thermoelectric properties of $BaSi_2$ by controlling the carrier concentration. We prepared polycrystalline samples of La-doped $BaSi_2$ and $(Ba,Sr)Si_2$ solid solutions. The electrical resistivity (ρ), Seebeck coefficient (S) and thermal conductivity (κ) were evaluated from room temperature to 973 K, and the ZT (= $S^2T/\rho/\kappa$) was calculated. 3 at.% La doing increased the carrier concentration, leading to enhancement of ZT (0.07 at 970 K). [1] V. K. Zaitsev, M. I. Fedorov, E. A. Gurieva, I. S. Eremin, P. P. Konstantinov, A. Yu. Samunin, and M. V. Vedernikov, Phys. Rev. B 74 (2006) 045207. [2] K. Hashimoto, K. Kurosaki, Y. Imamura, H. Muta, and S. Yamanaka, Proceedings of the 26th International Conference on thermoelectric, (2007), submitted.

U6.13

Crystal Growth of Mg2Si by the Vertical Bridgman Method and the Doping Effect of Bi and Al on Thermoelectric Characteristics. Masataka Fukano, Tsutomu Iida, Masayasu Akasaka, Noriaki Kato, Yohei Oguni and Yoshifumi Takanashi; Materials Science and Technology, Tokyo University of Science, Noda-shi, Chiba, Japan.

Magnesium silicide (Mg2Si) has been regarded as a candidate for advanced thermoelectric materials, for use in the temperature range from 500 to 800 K, corresponding to the temperature of vehicle exhaust emissions. In addition, the constituents of Mg2Si have the benefits of being abundant in the earth's crust and are non-toxic, compared with other thermoelectric materials that operate in the above conversion temperature range, such as PbTe and CoSb3. The efficiency of a thermoelectric device is characterized by the dimensionless figure of merit, ZT=S2sT/k, of its constituent thermoelectric material, where S is the Seebeck coefficient, s is the electrical conductivity, k is the thermal conductivity, and T is the absolute temperature. For thermoelectric device operation, the use of a material with ZT greater than unity is needed to realize a conversion efficiency of ~10 %. The optimization of the doping carriers in Mg2Si is required in order to realize unity of ZT. In this manner, we have grown Mg2Si crystals, doped with Bi and Al, using the vertical Bridgman method. Mg (99.99 %) and Si (99.99999 %) with a stoichiometric Mg : Si ratio of 67 : 33 were mixed and melted into Mg2Si. Prior to the growth, Bi (99.999 %) powder, at the ratio from 0.5 to 3 at. % with Mg2Si and a pre-synthesized polycrystalline Mg2Si powder were mixed. Mg2Si crystals were then grown at a rate of 3 mm/h using the vertical Bridgman method. Grown samples were characterized by x-ray diffraction (XRD) patterns and electron-prove microanalysis (EPMA), and the results indicated that Mg2Si crystals were successfully grown through their use of polycrystalline Mg2Si as a growth source material. Hall carrier concentrations were evaluated at room temperature. The electrical conductivity, the Seebeck coefficient, and the thermal conductivity were estimated in the temperature range from RT to 850 K. The grown crystals exhibited n-type conductivity in undoped and all Bi doped conditions. All the Bi doped crystals showed high electrical conductivity and high carrier concentration than seen in the undoped crystals. On the other hand, the thermal conductivity was lowered in proportion to the concentration of Bi. Consequently, the thermal conductivity of the crystals, Bi doped at 3 at. %, was 0.021 W/cmK at 842K, with a ZT attaining 0.99 at 842 K, close to the unity value of ZT that is regarded as a standard for practical use of thermoelectric materials. The solid solubility limit of Bi in Mg2Si was assumed to be around 3 at. % from our findings, and thus Al was co-doped with Bi in order to further improve the thermoelectric properties.

U6.14

Doping Characteristics of Silver in Mg2Si(1-x)Gex Prepared by Plasma Activated Sintering. Junichi Sato[1], Takashi Nemoto[1], Tsutomu Iida[2], Masayasu Akasaka[2], Atsunobu Matsumoto[2], Tadao Nakajima[1], Keishi Nishio[2] and Yoshifumi Takanashi[2]; [1]Nippon Thermostat Co., Ltd., Kiyose-shi Tokyo, Japan; [2]Department of Materials Science and Technology, Tokyo University of Science, Noda-shi Chiba, Japan.

As one of relevant solutions to remedying the Greenhouse effect, demands to reduce the usage of fossil fuels have been increasing. Since the immediate abstaining from the use of fossil fuels is impossible to attain in the near future, a remarkable increase in the energy conversion efficiency of combustible power generators is required. Mg2Si and Mg2Si1-xGex are promising candidates as thermal-to-electric energy-conversion materials, at operating temperatures ranging from 500 to 800 K. One important aspect of Mg2Si and Mg2Si1-xGex is the non-toxicity of source materials and processing by-products, which provides safe handling with no concerns regarding potential extended restrictions on hazardous substances. With Bi-doped n-type Mg2Si, we have achieved a maximum value of dimensionless figure-of-merit, ZT, of ~1.0 at ~ 850 K. In order to realize a Mg2Si thermoelectric power generator, a combination structure, consisting of n- and p-type Mg2Si, would appear to be more efficient in terms of space utility and output power density. However, stable doping parameters to produce p-type conductivity in Mg2Si have not yet been successfully extracted. On the other hand, doping is readily facilitated in p-type Mg2Si1-xGex. Moreover, Mg2Si1-xGex possesses a lower thermal conductivity, compared with Mg2Si, thus it can be expected to achieve a higher ZT value. In this report, we describe the doping characteristics of silver (Ag) in Mg2Si1-xGex (x=0.1 to 0.4), fabricated by plasma activated sintering (PAS). The doping concentration of Ag was varied from 1 to 5 at.%. In the present experiment, composition x was varied, only from 0.1 to 0.4, mainly because the Ge rich content results in degradation at an elevated operational temperature of ~ 800 K. Typically, undoped Mg2Si1-xGex in our fabrication process exhibits n-type conductivity for $x \le 0.4$, due to residual impurities in the Mg source material used and process-induced unintentional impurities. This seems to bring about an unstable behavior in the Seebeck coefficient of Ag-doped p-type Mg2Si1-xGex ($x \le 0.3$) in the region 550 to 650 K, indicating a considerable drop in the value and occasional conduction type conversion. For x~0.4, the observed Seebeck coefficient was 0.2 mV/K at 823 K to 0.4 mV/K at room temperature, with no remarkable drop in the value with increasing the temperature. The estimated ZT value for 5 at.% Ag doped Mg2Si0.6Ge0.4 was 0.18 at 844 K. It was found that the specific residual impurities and process-induced impurities affected the considerable drop in the Seebeck coefficient of Mg2Si1-xGex close to the anticipated operational temperature. Reduction of the unintentional impurities contributed to the achievement of linear variation in the Seebeck coefficient with temperature, and improved ZT values of 0.30 at 873 K for 3 at.% Ag doped Mg2Si0.6Ge0.4, indicating a doping efficiency improvement by reducing compensation from unintentional donor impurities.

U6.15

Fabrication of Mg2Si from a Reused-silicon Source and its Thermoelectric Characteristics. Masayasu Akasaka[1,3], Tsutomu Iida[1], Yohhiko Mito[2], Takeru Omori[1], Yohei Oguni[1], Shigeki Yokoyama[2], Keishi Nishio[1] and Yoshifumi Takanashi[1]; [1]Department of Material Science and Technology, Tokyo University of Science, Noda, Japan; [2]Showa KDE Co. LTD, Tokyo, Japan; [3]Research Fellow of the Japan Society for the promotion of Science, Tokyo, Japan.

The recent transition in the rate of global warming and the increase in global demand for energy have heightened the need for alternative energy sources to replace fossil fuels. The use of thermoelectric technology to convert waste heat energy directly into electrical energy has been proposed as a possible technology to reduce our dependence on fossil fuels and to reduce greenhouse gas emissions. Magnesium silicide (Mg2Si) has been identified as a promising advanced thermoelectric material operating in the temperature range from 500 to 800 K. Compared with other thermoelectric materials that operate in the same conversion temperature range, such as PbTe and CoSb3, some important characteristics of Mg2Si are that it has been identified as an environmentally-friendly material, its constituent elements are abundant in the earth's crust, and it is non-toxic. In order to realize thermoelectric devices that are based on Mg2Si, along with improvements in its thermoelectric properties, cost reductions of the source materials and manufacturing processes are also required. Here we have tried to introduce reusing of Si as a source material for Mg2Si, because the current product inversion rate of Si for semiconductor devices remains at 30 to 40 %, while most of the remainder is disposed of as an industrial waste; this is mainly discharged as sludge from grinding and polishing processes. It is possible that the reuse of this waste Si could be effective in both reducing the cost of source Si and in the reduction of industrial waste. Since the Si sludge is covered with a native oxide, the refining treatment has to be conducted under a reducing atmosphere to remove the oxide. Mg (99.95%) and the reduced Si were pre-synthesized at

a stoichiometric ratio (Mg : Si = 2 : 1), and then Mg2Si was sintered from the resulting polycrystalline Mg2Si using a plasma activated sintering method. In order to improve the thermoelectric properties, Bi or Ag were added as an n-type dopant or a p-type dopant respectively. The Seebeck coefficient, the electrical conductivity and the thermal conductivity were investigated over the temperature range from RT to 850 K. The thermoelectric properties of Mg2Si using reused-Si were comparable to those of Mg2Si produced from high purity Si (99.99999%), while those of Bi-doped Mg2Si produced using reused-Si were superior to those of Mg2Si from high purity Si. The dimensionless figure of merit, ZT, for a sample produced using reused-Si that was doped with Bi at 2 atoms % reached 0.6 at 840 K. The theoretical thermoelectric properties of Mg2Si have not been investigated sufficiently so far, and thus these have been calculated from first principles using a Local Density Approximation (LDA) by the all-electron Full potential Linearized Augmented Plane Wave (FLAPW) method. The calculated values were compared with the measured values, and the calculated thermoelectric properties of the material were found to be comparable with the measured values.

U6.16
Abstract Withdrawn

U6.17
Effect of Combined Addition of Silicon Carbide Whiskers and Fullerene Nanoparticles on Properties of Thermoelectric Zinc Antimonite.
Takashi Itoh[1], Nobuhisa Asari[1], Nobuyuki Kanetake[2] and Akira Okada[3]; [1]EcoTopia Science Institute, Nagoya University, Nagoya, Japan; [2]Materials Science and Engineering, Nagoya University, Nagoya, Japan; [3]Nissan Research Center, Nissan Motor Co. Ltd., Yokosuka, Japan.

Thermoelectric power generation is a hopeful method harnessing waste thermal energy particularly covering a middle temperature range between 500 and 800K. A Zn4Sb3 compound is a promising "phonon glass electron crystal" material applicable to thermoelectric power generation around 700K. This material, however, has a problem of its brittleness. In this research, the silicon carbide whiskers were added into the Zn4Sb3 compound for overcoming the brittleness, and the fullerene nanoparticles were also added for improving the thermoelectric performance. The Zn4Sb3 compound was synthesized from mixture of pure zinc and antimony powders by a liquid-solid phases reaction method. Firstly, the synthesized compound powder was mixed with the fullerene nanoparticles. The planetary ball milling method was used in order to disentangle the fullerene agglomerate and to obtain a uniform mixture. Subsequently, the mixture was uniformly mixed with the SiC whiskers by the planetary ball milling. The final mixture was consolidated by the pulse discharge sintering. The synthesized phases were identified by XRD. The morphology of the whiskers after mixing was observed. The flexural strength and the thermoelectric properties of the sintered samples were measured. The length of SiC whiskers and the flexural strength were decreased with the mixing time. Though the addition of SiC whiskers lowered the thermoelectric performance, the combined addition of SiC whiskers and fullerene nanoparticles restored the performance by especially decrease of the thermoelectric conductivity owing to the phonon scattering.

U6.18
Optimization of Thermoelectric Properties of Ni-Cu based Alloy through Combinatorial Approach.
Atsushi Yamamoto, Haruhiko Obara and Kazuo Ueno; Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan.

Ni-Cu based alloys are well-known as materials used for thermocouples. The alloys have good electrical conductivity in the order of 10^{-7} ohm-m and relatively large Seebeck coefficient for metal, but a lack of low thermal conductivity excludes the materials from consideration as thermoelectric materials. From a thermoelectric classical consideration, we need to enhance figure of merit Z value to realize high performance thermoelectric conversion system. On the other hand, some earlier studies on thermoelectric system analysis pointed out that there is a possible way to realize high-efficiency power generating system using a highly thermally conducting material [1]. The main requirement for the materials used in such systems is high power factor value. Ni-Cu and related alloy could be one of the candidates for the high power factor materials. In this study, we demonstrate a combinatorial screening experiment on Ni-Cu and related materials by combining the use of bulk composition-spread samples prepared by powder metallurgy process and Scanning Thermal Probe Micro-analyzer, which can map out the Seebeck coefficient and the thermal conductivity simultaneously. The Ni-Cu binary alloy with optimized composition was found to possess power factor value of 0.012 $Wm^{-1}K^{-2}$ at 950K and further enhancement could be possible by conducting systematic experiments based on the combinatorial approaches performed in this study.
[1] R.Echigo, K.Hanamura, H.Yoshida, M.Koda, and K.Tawata, Proc. 11th Int. Conf. on Themroelectrics, (1992) 45.

U6.19
LSCO Ceramics as Possible Thermoelectric Material for Low Temperature Applications.
Julio E. Rodriguez, Physics, Universidad Nacional de Colombia, Bogotá, Colombia.

Seebeck coefficient, S(T) and electrical resistivity, ρ(T) on polycrystalline $La_{1.85}Sr_{0.15}CuO_{4+\delta}$ compounds were carried out in the temperature range between 100K and 290K. The samples were grown by conventional solid state reaction method; the thermoelectric properties of the samples were tuned by changing their oxygen content. The Seebeck coefficient is positive in the measured temperature range and its magnitude increases with the reduction of oxygen content up to reach values close to 120 μV/K. While the electrical resistivity, in all the samples took values less than 1mΩ-cm and a metallic behavior. From S(T) and ρ (T) data, the thermoelectric power factor (PF) of the samples was determined; it reaches values close to 18 $\mu W/K^2$-cm at 200K. The behavior observed in the transport properties become these compounds in promissory thermoelectric materials for low temperature applications.

U6.20
In-Plane Thermoelectric Properties of Polycrystalline Highly Preferred Orientation WSe2 Superlattice Thin Films.
Anastassios Mavrokefalos[1], Michael Thompson Pettes[1], Li Shi[1], Ngoc Nguyen[2] and David Johnson[2]; [1]Mechanical Engineering, University of Texas at Austin, Austin, Texas; [2]Department of Chemistry, University of Oregon, Eugene, Oregon.

It was recently found by using the time domain thermal reflectance method that polycrystalline highly preferred orientation WSe2 superlattice films possess extremely low cross-plane thermal conductivity, which is desirable for thermal insulation and thermoelectric energy conversion applications. However, it is difficult to obtain the in-plane thermal conductivity by using the laser reflectance or the 3-ω method. Here we employ a suspended

microdevice developed for measuring thermoelectric properties of individual nanowires to obtain the in-plane thermal conductivity, electrical conductivity, and Seebeck coefficient of WSe2 superlattice films. The measurement results show that the in-plane thermal conductivities of these films are much higher than the cross-plane values, making the thermal conductivity of the films highly anisotropic.

U6.21
Thermal and Electrical Transport Properties of Nano-Particles Added Half-Heusler Alloys. Vijayabarathi Ponnambalam, Sloan Lindsey, Paola N. Alboni, Brad Edwards and Terry M. Tritt; Dept. of Physics and Astronomy, Clemson University, Clemson, South Carolina.

As predicted by the theory, nano-particles added alloys of various materials have been reported to exhibit a reduction in the thermal conductivity up to ~ 40% without a substantial change in the electrical transport properties. Motivated by this result, we have investigated this effect in half-Heusler alloys, where we have added different kinds of particles with size ranging from submicron to few tenth of a nanometer by various methods. Measurements of thermal and electrical transport properties are underway. We will present the details of nano-composite synthesis techniques and the thermoelectric transport properties.

U6.22
Investigations of Bonding in Skutterudites by Electron Energy Loss Spectroscopy. Oystein Prytz[1], Ragnhild Saeterli[2], Randi Holmestad[2] and Johan Tafto[1]; [1]Department of Physics, University of Oslo, Oslo, Norway; [2]Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway.

The local electronic structure of Co in the binary skutterudites CoP_3, $CoAs_3$, and $CoSb_3$ has been investigated using EELS through comparisons of the $L_{2,3}$ energy-loss edges [1]. In skutterudites, the transition metal element is octahedrally coordinated by pnicogens, forming strong covalent bonds. Our investigations show a depletion of the Co 3d states in skutterudites compared to the pure Co-metal. Meanwhile, studies of Fe $L_{2,3}$ edges show charge transfer from La to Fe in $LaFe_4P_{12}$ [2], consistent with models of bonding in filled skutterudites. Furthermore, we report the study of phosphorus L-edges of filled and unfilled phosphorus-based skutterudites. Experimental EELS results are presented along with real space multiple scattering calculations using FEFF8.5 [3]. These investigations reveal that the $L_{2,3}$ edges of the tetrahedrally coordinated P shows great similarity to that of tetrahedrally coordinated Si. The experimental and theoretical energy loss spectra from the various phosphorus skutterudites are compared and discussed in light of the calculated local density of states. **References** [1] D. H. Pearson, C. C. Ahn, and B. Fultz. White lines and d-electron occupancies for the 3d and 4d transition metals. *Phys. Rev. B* **47**, 8471 (1993). [2] Ø. Prytz, J. Taftø, C. C. Ahn, and B. Fultz. Transition metal d-band occupancy in skutterudites studied by electron energy-loss spectroscopy. *Phys. Rev. B* **75**, 125109 (2007). [3] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson. Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure. *Phys. Rev. B* **58** (12), 7565 (1998).

SESSION U7: Nanocomposites III and Bulk Thermoelectrics II
Chairs: Ryoji Funahashi and Jeff Snyder
Wednesday Morning, November 28, 2007
Room 311 (Hynes)

8:30 AM U7.1
Reduced Thermal Conductivity by Low-Frequency Optic Phonons that Give Rise to Negative Thermal Expansion: Opportunities for Thermoelectrics? Mary Anne White and Catherine A. (Kennedy) Whitman; Dalhousie University, Halifax, Nova Scotia, Canada.

We have recently found that the negative thermal expansion (NTE) materials, ZrW2O8 and HfMo2O8, show exceptionally low thermal conductivity. We surmise that the mechanism is the efficient coupling of the low-frequency optic phonons that give rise to negative thermal expansion with the heat-carrying acoustic phonons. Although neither ZrW2O8 nor HfMo2O8 has suitable electronic properties for thermoelectric applications, perhaps the principle of reduced thermal conductivity by low-frequency optic phonons in NTE materials can be used to develop more efficient thermoelectric materials.

8:45 AM U7.2
Effect of $CoSb_3$ Nanoparticles on Filled and Unfilled $CoSb_3$ Skutterudites. Paola N Alboni, X. Ji, N. Gothard, J. He and T. M. Tritt; Physics & Astronomy, Clemson University, Clemson, South Carolina.

The effects of nanoparticles that were hydrothermally grown on the surface of bulk powders of several skutterudite materials were studied and the results are presented in this paper. Both filled and unfilled $CoSb_3$ skutterudites were grown and then emersed in a hydrothermal solution where $CoSb_3$ nanoparticles were grown. Similar compositions were used for the bulk materials and the nanoparticles in an attempt to effectively reduce thermal conductivity while keeping electronic properties relatively intact. The electronic and thermal properties of these materials including thermal conductivity, thermopower and electrical resistivity, were measured from 10K to 600K and the results and analysis are presented herein.

9:00 AM U7.3
Thermal And Electronic Transport In Rare-Earth Ruthenium Germanium Compounds. Donald T. Morelli[1], H. Kong[2], X. Shi[2] and C. Uher[2]; [1]Dept. of Chem. Eng. & Materials Sci., Michigan State University, East Lansing, Michigan; [2]Dept. of Physics, University of Michigan, Ann Arbor, Michigan.

We report our studies of the thermoelectric properties of a class of compounds of composition R3Ru4Ge13 (R = Y, Dy, Ho, and Lu). Magnetization measurements show that the R ion is in the trivalent state in each of these compounds. Each of these compounds displays a semiconductor-like rise in electrical resistivity with decreasing temperature. The magnitude of the resistivity is much larger than typical metals and is similar to that of a heavily-doped semiconductor or semimetal. The Seebeck coefficient is positive throughout the temperature range 2K - 800 K with room temperature

values of approximately 40 μV K-1. The lattice thermal conductivity is remarkably low and exhibits a very flat temperature dependence. This is consistent with the observed internal disorder associated with the cage-like structure of these compounds. Cobalt substitution for ruthenium enhances the semiconductor character but does not improve the thermoelectric properties.

9:15 AM U7.4

Preparation and Characterization of High Temperature Thermoelectrics Based on Metal/Oxide Nanocomposites. Otto J. Gregory[1], Ximing Chen[1] and Gustave Fralick[2]; [1]Chemical Engineering, Univ. of Rhode Island, Kingston, Rhode Island; [2]NASA Glenn Research Center, Cleveland, Ohio.

Thermoelectric devices based on "n-type" oxide semiconductors and metal/oxide (cermet) nanocomposites are being considered for high temperature thermocouples and heat flux sensors as well as other energy harvesting devices. In terms of energy harvesting, considerable electrical energy can be generated from the large thermal gradients that exist within the gas turbine engine environment. Several promising bi-ceramic junctions were systematically investigated for their high temperature thermoelectric properties including a promising one based on indium tin oxide (ITO) and a NiCrCoAlY/alumina nanocomposite, whose individual thermoelectric responses were initially evaluated relative to a platinum reference electrode. A maximum emf of 90mV was realized for a NiCrCoAlY/alumina nanocomposite-platinum couple when a temperature gradient of 1026°C and hot junction temperature of 1100°C were employed. The Seebeck coefficient for this couple was 230μV/°C. When similar nanocomposites were combined with ITO to form bi-ceramic junctions, Seebeck coefficients on the order of ~750μV/°C were obtained with reproducible voltage/temperature behaviour after repeated thermal cycling. For these bi-ceramic junctions, a maximum emf of 300mV was achieved for a hot junction temperature of 1100°C. The sputtering conditions including N2, O2 and Ar partial pressure used to deposit the ITO had a large effect on the thermoelectric response and Seebeck coefficient of the bi- ceramic junctions. The thermoelectric response and Seebeck coefficient decreased with increasing nitrogen partial pressure in the plasma when the partial pressures of oxygen and argon were held constant. The relationship between the sputtering process parameters and the resulting thermoelectric properties were investigated and the implications of these materials in thermocouples and energy harvesting devices is discussed.

9:30 AM U7.5

Development of Double-Gyroid Topology Nanowire Array Thermoelectric Devices. Hugh W Hillhouse, School of Chemical Engineering, Purdue University, West Lafayette, Indiana; The Energy Center, Purdue University, West Lafayette, Indiana.

The use of nanowires provides intriguing possibilities for increasing the figure of merit for thermoelectric power generation due to quantum size effects and enhanced phonon scattering. However, for materials such as PbTe and other chalcogenide materials, these possibilities have not yet been investigated due to the difficulty in synthesizing nanowires of sufficiently small diameter, high perfection and high purity. Further, practical devices must be based on large arrays of nanowires of sufficient length. Here, the presentation will focus on our recent development of large arrays of 4 nm diameter PbTe nanowires and PbTe nanowire-based thermoelectric devices. These unique nanomaterials are fabricated using highly ordered nanoporous films as a nanowire template. A key step in this fabrication process is our recent development [1] of self-assembled nanoporous films with suitably small diameter pores that provide direct access an underlying stainless steel electrode through the nanopore. The nanoporous films are highly oriented and ordered. 2D grazing incidence small-angle x-ray scattering (GISAXS) results in 96 diffraction peaks that can all be indexed with a (211) oriented film that exhibits systematic extinctions based on Ia-3d symmetry. Comparison of observed and simulated transmission electron microscopy (TEM) images show that the pore topology is based on the zero mean curvature G-surface (the tricontinuous "double-gyroid" topology) with a pore diameter of approximately 4 nm. These nanoporous film coated electrodes have been filled by electrochemical deposition of PbTe with high fidelity. The pore fill fractions are over 80%, and the PbTe nanowire array films are opaque, black in color, crack-free and uniform in appearance. GISAXS and TEM images of the PbTe/SiO2 nanostructured hybrids and of the free standing PbTe nanowire arrays show that that the PbTe has the topology of the inverse double-gyroid - 4 nm diameter PbTe nanowires interconnected with Ia-3d symmetry. The presentation will focus on the synthesis and characterization of the nanostructured thermoelectric layer, device fabrication, and thermoelectric performance evaluation using an AC electrical measurement technique [2]. References: [1] Urade VN, Wei TC, Tate MP, Kowalski JD, & Hillhouse HW, "Nanofabrication of double-gyroid thin films," Chem. Mater. 19 (4), 768 (2007). [2] Downey AD, Hogan TP, "Circuit Model of a Thermoelectric Module for AC Electrical Measurements," IEEE Proceedings of the 2005 International Conference on Thermoelectrics, p. 79-82.

9:45 AM U7.6

Thermoelectric Properties of Nearly Single-Phase Half-Heusler NbCoSn Alloys and Importance of Microstructures for Improving Performance. Yoshisato Kimura[1], Yukio Tamura[1] and Takuji Kita[2]; [1]Materials Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan; [2]Higashifuji Technical Center, Toyota Motor Corporation, Susono, Japan.

Thermoelectric power generation is one of solutions that are helpful to conserve the global environment. We have been focusing on half-Heusler compounds which can be used to directly convert waste heat to clean electric energy at high temperatures around 800 to 1000 K. It is well-known that half-Heusler compounds with the valence electron counts of 18 show semi-conducting behavior. Many research groups including us have paid much attention on n-type MNiSn (M = Ti, Zr, Hf) system since MNiSn based alloys possess high potential of thermoelectric performance. As we have widely investigated Sn-based half-Heusler compounds, our attention is placed on n-type NbCoSn in the present work. Fabrication of monolithic NbCoSn is very difficult like other half-Heusler systems, because melting point of Sn is too much low comparing with other constituent elements. We have successfully fabricated nearly single-phase NbCoSn alloys by means of directional solidification (DS) using optical floating zone (OFZ) method in an argon gas flowing atmosphere under a slightly positive pressure. In order to understand the effects of coexisting phases on thermoelectric properties of NbCoSn, two-phase alloys were also prepared by OFZ-DS method. Coexisting metallic phases with NbCoSn phase are; Nb_3Sn at the Co-lean side and $NbCo_2Sn$ at the Co-rich side, from the stoichiometric composition of NbCoSn. Single-phase NbCoSn alloy shows the highest thermoelectric power among NbCoSn based alloys prepared in this work, and its maximum value is exceeding -250 μV/K at around 900 K. On the other hand, electrical resistivity of single-phase NbCoSn alloy is higher than others, which is consistent with the largest thermoelectric power. Carrier concentration of single-phase NbCoSn alloy, 4.83×10^{-26} m^{-3}, slightly increases due to coexisting metallic phases in two-phase alloys. Note that NbCoSn seems to exhibit semi-metallic behavior rather than semi-conducting behavior, judging from the propensity of temperature dependence of electrical resistivity increasing with temperature. As we have expected, single-phase NbCoSn alloy has the most excellent power factor among these alloys, 2.5 $mWm^{-1}K^{-2}$ at about 650 K. It is 1.5 times larger than two-phase alloys, and 3 times higher than hot-pressed counterpart with multi-phase microstructure. These are very important results that electrical properties are quite susceptible to microstructures of alloys, and that excellent power

factor can be achieved without any tuning of electrical properties through optimizing carrier concentrations. Thermal conductivity of single-phase NbCoSn alloy stays almost constant at relatively high values around 6 $Wm^{-1}K^{-1}$, typical of half-Heusler compounds, in the entire measured temperaturesup to 1100 K. Consequently, the maximum value of figure of merit ZT is achieved in single-phase NbCoSn alloy, ZT = 0.3 at 984 K, which is 1.5 to 2.0 times higher than other multi-phase alloys.

10:30 AM *U7.7

Theoretical Study of Thermoelectric Response in Strongly Correlated Electron Systems. Wataru Koshibae, Sendai National College of Technology, Sendai, Japan.

We have studied the effects of spin and orbital degrees of freedom in the strongly correlated electron systems, and have derived the formula of the high-temperature thermopower: Q = - (k_B/e)ln (g_e/g_h) - (k_B/e)ln [n_h/(1 - n_h)], (1) where n_h is the hole concentration, and g_e (g_h) denotes the local degeneracy of the electronic configuration on the transition metal ion without (with) hole carrier. The local degeneracy is determined by the spin and orbital degrees of freedom. It has been established that the formula (1) gives a good estimation of the thermopower in not only the 3d transition metal oxides but also the 4d ones, recently. We have studied the thermopower in the oxides composed of several kinds of transition metal ions. Its high-temperature formula shows a complicated expression, however, it is expressed to be the average of the first term of the equation (1) in the case that n_h = 0.5, in the double perovskite system. This is because the thermopower is nothing but the entropy carried by the electric current. We will discuss the thermopower of the oxides with several kinds of transition metal ions in the light of the theory. The cobalt oxide, Na_xCoO_2, shows not only a large thermoelectric response but also an anomalous high-temperature Hall effect: The Hall coefficient increases linearly as a function of temperature and the magnitude comes to no fewer than 8 times as large as the expected Drude value. On the electron system with the large thermopower and the large Hall coefficient, an interesting behavior is expected in the response to a magnetic field upon a temperature gradient. We have studied the electronic state of the cobalt oxide and found that the electronic structure reflects the nature of the Kagome lattice hidden in the CoO_2 layer. We will show the importance of the hidden Kagome lattice structure in the emergence of the anomalous Hall effect and the close relation between the Hall and Nernst coefficients.

11:00 AM U7.8

Abstract Withdrawn

11:15 AM U7.9

Thermoelectric Oxides and Oxynitrides with Perovskite-type Structure. Anke Weidenkaff[1], Myriam H. Aguirre[1], Rosa Robert[1], Laura Bocher[1], Dmitry Logvinovich[1], Andrey Shkabko[1] and Stefan Ebbinghaus[2]; [1]Solid State Chemistry and Catalysis, Empa-Swiss Federal Laboratories for Materials Testing and Research, Duebendorf, Switzerland; [2]University of Augsburg, Augsburg, Germany.

Transition metal oxides with perovskite-type structures are potential high temperature stable thermoelectric materials [1]. It was previously found that lowering the dimensions of thermoelectric materials to the nanome-ter scale leads to a significant enhancement of the thermoelectric properties [2]. Thus, very high values for the figure of merit, ZT (ZT > 2) have been reported for nanoscaled systems such as superlattices and quan-tum dots [3]. However, it is well known that the material starts to sinter when heated. Thus, sinter-stable high surface area ceramics are required to maintain the good thermoelectric properties at high temperatures. With innovative soft chemistry synthesis procedures the crystallite size in complex oxide ceramics with perovskite-type structure can be decreased compared to classical synthesis routes and allows to lower the heat conductivity dramatically while a large power factor can be maintained at the same time. Studies on boundary scattering of phonons indicate that submicron crystallites are beneficial to lower the lattice thermal conductivity without influencing the electron mobility. In this work, perovskite-type nickelates, cobaltates, titanates, and manganates are studied. Three levels of structural analysis will be presented: atomic structure, nanostructural texture and microstructural morphology. For this purpose, high resolution transmission electron microscopy and -scanning electron microscopyare performed. The influence of heterostructures and nanocrystalline domains in perovskite oxides/oxynitrides thin epitaxial films and the correlation with transport properties and Seebeck coefficient will be discussed. <p> [1] R. Robert, L. Bocher, M. Trottmann, A. Reller, A. Weidenkaff, J. of Solid State Chem. 179, 3893 (2006). [2] L. Hicks, M. Dresselhaus, Phys. Rev. B47, (1993) 12727 [3] Y. Lin, X. Sun, M. Dresselhaus, Phys. Rev. B62 (2000) 4610, and Y. Lin, S. Cronin, J. Ying, M. Dressel-haus, J. Heremans, Appl. Phys. Lett. 76 (2000) 3944.

11:30 AM U7.10

Thermoelectric and Mechanical Properties of $Ca_{0.9}Yb_{0.1}MnO_3$ Based Materials. Atsuko Kosuga[1], Saori Urata[2] and Ryoji Funahashi[1,2]; [1]National Institute of Advanced Industrial Science and Techology (AIST), Ikeda, Osaka, Japan; [2]CREST, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

$CaMnO_3$ based materials are good candidates for n-type legs of thermoelectric modules in air. In our previous studies, various doping and microstructural control were attempted to improve the thermoelectric properties of $CaMnO_3$ based materials. As a result, a polycrystalline sample of $Ca_{0.9}Yb_{0.1}MnO_3$ was found to exhibit a quite high ZT : 0.16 at 1000 K in air [1]. Moreover, thermoelectric modules were prepared using $CaMnO_3$ based bulks. However, they were broken by heating due to their low mechanical strength [2]. In this study, Ag particles were dispersed into the $Ca_{0.9}Yb_{0.1}MnO_3$ matrix to fabricate mechanically strengthened materials with improved thermoelectric performance. The $Ca_{0.9}Yb_{0.1}MnO_3$/Ag composites were prepared by wet ball milling various weight ratios of Ag_2O to $Ca_{0.9}Yb_{0.1}MnO_3$ powder in ethanol for 48 h. The resulting compositions contained 0-20 wt% Ag after sintering. The samples were sintered in the temperature range from 1273 to 1673 K for 2 h in air. Bulk density was calculated based on the measured weight and dimension of each sample. The phase identification was performed by a powder X-ray diffraction (XRD) method carried out at room temperature using Cu-Kα radiation. The microstructure was observed with a scanning electron microscopy (SEM). The effect of Ag contents on the thermoelectric and mechanical properties of $Ca_{0.9}Yb_{0.1}MnO_3$/Ag composites will be discussed. [1] D. Flahaut et al., J. Appl. Phys. 100, (2006) 084911-1. [2] S. Urata et al., Proceeding of 2006 International Conference on Thermoelectrics, (2007) 501.

SESSION U8: Chalcogenides II, Thin Films and Thermionics

Chairs: Jeff Sakamoto and Ctirad Uher
Wednesday Afternoon, November 28, 2007
Room 311 (Hynes)

1:30 PM U8.1
Transport Behavior, Thermal Conductivity Reduction, and Improved Thermoelectric Performance in the Composite System PbTe - Pb -Sb.
Joseph R. Sootsman[1], Huijun Kong[2], Ctirad Uher[2], Adam Downey[3], Jonathan James D'Angelo[3], Chun-I Wu[3], Timothy P. Hogan[3], Thierry Caillat[4] and Mercouri G. Kanatzidis[1]; [1]Department of Chemistry, Northwestern University, Evanston, Illinois; [2]Department of Physics, University of Michigan, Ann Arbor, Michigan; [3]Department of Electrical and Computer Engineering, Michigan State University, East Lanstin, Michigan; [4]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Thermoelectric materials may be useful in heat to electrical energy conversion technology if their efficiencies can be improved. We report the synthesis of nanostructured composite PbTe with excess Pb and Sb metal inclusions. Scanning and transmission electron microscopy reveal these inclusions in both the nano- and macroscales. Electrical and thermal transport measurements show these composites can be tuned by the ratio of excess Pb/Sb. Unique transport behavior, as a result of modified carrier scattering, is observed is samples with an optimum Pb/Sb ratio. Hall coefficient measurements show the mobility of these composites no longer follow typical temperature dependence ($\mu \sim T^{2-2.5}$). This results in improved electrical conductivity at high temperature and higher power factors than those of PbTe with similar carrier concentration. The thermal conductivity of these composites also reiterates that nanostructured bulk materials have reduced thermal conductivity if the nanoscale features are chose appropriately. Through the reduction of thermal conductivity and increased power factors optimized samples give the improved ZT of 1.4 at 675K.

1:45 PM *U8.2
Thallium-Free Thermoelectric Materials with Extremely Low Thermal Conductivity.
Shinsuke Yamanaka, Ken Kurosaki, Anek Charoenphakdee, Hideaki Matsumoto and Hiroaki Muta; Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Japan.

With the goal of developing high-performance bulk thermoelectric materials, we have characterized ternary silver thallium tellurides. The ternary silver thallium tellurides exhibit extremely low thermal conductivity (<0.5 $Wm^{-1}K^{-1}$) and consequently their thermoelectric performance is excellent. Although the extremely low thermal conductivity materials, as typified by the ternary silver thallium tellurides, would be a new class of next-generation thermoelectric materials, thallium compounds are unsuitable for practical application because of their toxicity. Against such a background, we are currently exploring thallium-free thermoelectric materials with extremely low thermal conductivity. Now we can propose two candidates: Ag_8GeTe_6 and Ga_2Te_3. Both materials exhibit quite low thermal conductivity, e.g. the values at room temperature are 0.26 and 0.57 $Wm^{-1}K^{-1}$ for Ag_8GeTe_6 and Ga_2Te_3, respectively. We will discuss the electrical transport properties as well as the thermal conductivity of these materials.

2:15 PM U8.3
Crystal Growth and Thermoelectric Properties of the Low-Dimensional Bismuth Selenides, $K_{1+x}Pb_{4-2x}Bi_{7+x}Se_{15}$ and $Cs_{1-x}Pb_{4-x}Bi_{11+x}Se_{21}$.
Duck-Young Chung[1], Iliya Todorov[1] and Mercouri Kanatzidis[2,1]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [2]Department of Chemistry, Northwestern University, Evanston, Illinois.

The chemical system including alkali metal, bismuth and chalcogen possesses highly attractive structural features and favorable properties that could lead to thermoelectric materials with high ZT as has been shown for $CsBi_4Te_6$, and β-$K_2Bi_8Se_{13}$. A variety of combinations involving two simple building units (NaCl and Bi_2Se_3 type) in this system leads to a diversified set of structures that can be organized into a grand homologous series, $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$ (A = alkali metal, M = Sn, Pb, Sb, Bi). Also, their large unit cell with significant atomic mass contrast and disorder can lead to effective phonon scattering and their structural complexity may result in complex electronic structure near Fermi energy, both of which contribute to low thermal conductivity and high thermopower. We will present two promising thermoelectric materials $K_{1+x}Pb_{4-2x}Bi_{7+x}Se_{15}$ and $Cs_{1-x}Pb_{4-x}Bi_{11+x}Se_{21}$ which belong to the homologous series. The small single crystal samples of these compounds have shown 260 S/cm and -150 μV/K, 160 S/cm and -56 μV/K, respectively, at room temperature. We will report on the properties of large highly oriented crystals of these materials and present their thermoelectric properties. We will compare the data with those of for the small single crystal samples. Also, we will discuss chemical manipulations attempted to improve their properties.

2:30 PM U8.4
Thermoelectric Properties of Mixed-Metal Tellurides.
Anthony V Powell[1], Fabien Guinet[1], Paz Vaqueiro[1], Ian M Wilcock[2] and Richard L Jones[2]; [1]Chemistry, Heriot-Watt University, Edinburgh, United Kingdom; [2]Physical Sciences, DSTL, Salisbury, United Kingdom.

Thermoelectric materials offer unique opportunities for the construction of solid-state devices for refrigeration and power generation. The necessary combination of a high electrical conductivity (σ), low thermal conductivity (κ), and large Seebeck coefficient (S) required for high performance imposes considerable demands on materials design. This has led to a recent resurgence of interest in exploratory synthesis of chemically complex phases for thermoelectric applications. Recent reports [1] indicate that mixed-metal tellurides related to PbTe exhibit promising thermoelectric properties, with n-type $AgSbPb_mTe_{m+2}$, possessing ZT values as high as 2.2 for m=18 at 800K. Here, we will present the results of our recent investigations of complex metal tellurides, which have led [2] to a new series of thallium-containing materials, $Tl_{1-x}MPb_mTe_{m+2}$ ($0 \le x \le 0.3$; $10 \le m \le 18$; M=Bi, Sb). Powder X-ray and neutron diffraction data indicate a rocksalt-type structure is adopted at all compositions. Transport property measurements reveal that all materials are p-type semiconductors. Thallium deficiency leads to increased power factors for materials with x>0. Measured thermal conductivities are low, in the region of 1 $Wm^{-1}K^{-1}$, suggesting that these materials may have promise as p-type counterparts to $AgSbPb_mTe_{m+2}$ in device applications. We will also describe extensions of our investigations of complex metal tellurides, which have focused on

materials related to $PbBi_2Te_4$. In particular, we have explored chemical substitution at both the Pb and Bi sites, through preparation of series of materials of general formula $Pb_{1-x}A_xBi_{2-y}B_yTe_4$ (A=Sn, Ge; B= Sb). These materials adopt a layered structure in which triple octahedral blocks are separated by a van der Waals' gap, thereby affording the possibility to achieve enhancements of the density of states at the Fermi surface through spatial confinement of the electrons. References 1. K.F. Hsu et al, *Science* , 303, 818, (2004). 2. A.V. Powell et al, UK Patent Application GB0705779.7.

2:45 PM U8.5

Thermoelectric Properties of the Nanostructured $NaPb_{18-x}Sn_xMTe_{20}$ (M=Sb, Bi) Materials. Aurelie Gueguen[1,2], Pierre Ferdinand Poudeu Poudeu[1], Robert Pcioneck[2] and Mercouri G. Kanatzidis[1]; [1]Chemistry, Northwestern University, Evanston, Illinois; [2]Chemistry, Michigan State University, East lansing, Michigan.

Recently, we reported a record high thermoelectric figure of merit for the p-type material $Na_{1-x}Pb_mSb_yTe_{m+2}$. It was argued that the excellent thermoelectric properties derive from the extremely low lattice thermal conductivity resulting from the nanometer scale features embedded in the matrix as revealed by the high-resolution transmission electron microscopy images. Several samples with the general composition $NaPb_{18-x}Sn_xMTe_{20}$ (x=0, 2, 5, 9 13, 16, 18; M = Sb, Bi) were prepared in order to investigate the impact of partial substitution of lead by tin and the influence of the nature of the pnictide on the thermoelectric properties of the system. X-ray powder diffraction confirmed the cubic NaCl-type structure for all compositions. High resolution transmission electron microscopy of several specimens from selected compositions revealed the presence of nanometer scale features dispersed inside the matrix. The electrical conductivity of $NaPb_{18-x}Sn_xMTe_{20}$ compounds at 300K increases with decreasing Pb/Sn ratio whereas the thermopower decreases. All samples showed p-type behavior. The lattice thermal conductivity of the sample with composition $NaPb_{13}Sn_5SbTe_{20}$ decreases from ~1.3 W/m/K at 325K to about 0.8W/m/K at 575K. The electrical conductivity of the $NaPb_{18-x}Sn_xMTe_{20}$ materials seems to be very sensitive to the nature of M (Sb, Bi) as samples containing bismuth systematically exhibit lower electrical conductivity than the antimony analogs whereas no significant change is observed on the thermopower.

3:30 PM U8.6

Growth of Stoichiometric $Ba_8Ga_{16}Ge_{30}$ Films by Dual-Laser Ablation and Study of Growth Dynamics by Emission Spectroscopy. Robert H. Hyde, Pritish Mukherjee, Matthew Beekman, George S. Nolas and Sarath Witanachchi; Physics, University of South Florida, Tampa, Florida.

We have previously demonstrated the growth of crystalline thin films of the type I clathrate $Ba_8Ga_{16}Ge_{30}$ by the laser ablation process. However, films contained high density of particulates that were ejected from the clathrate target. In order to produce particulate free films we have used a dual-laser ablation process where the ablation was carried out by combining the pulses of excimer and CO_2 lasers that were temporally synchronized. The effect of the CO_2 laser energy on the target morphology and the stoichiometric removal of material from the target have been investigated. In addition, emission spectroscopic and time-gated CCD imaging techniques have been used to monitor expansion profiles of each element in the ablation plume. Through these investigations we have optimized the growth parameters to significantly reduce the particulate density on films and to produce uniform stoichiometric films over a large area of the substrate. Films deposited on silicon substrates were polycrystalline while those deposited on closely lattice matched single crystal yttrium stabilized zirconium (YSZ) substrates showed preferred orientation. Temperature dependant electrical conductivity and mobility of polycrystalline and oriented films will be presented.

3:45 PM U8.7

Rocksalt Structured Nitride Metal/Semiconductor Superlattices for Thermionic Energy Conversion. Vijay Rawat[1,2], Robert Wortman[3,2] and Tim Sands[1,3,2]; [1]School of Materials Engineering, Purdue University, West Lafayette, Indiana; [2]Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana; [3]School of electrical and computer engineering, Purdue University, West Lafayette, Indiana.

Moderate to high temperatures (400 - 1000 oC) present significant challenges in the selection and design of thermoelectric materials for devices that directly convert a temperature difference into electric power. In particular, the advances in the materials figure of merit, ZT, that have been attained using nanostructured materials have largely been confined to lower operating temperatures. To exploit the potential of nanostructured materials at higher temperatures, it is necessary to identify materials that can maintain nanoscale features at moderate to high temperatures such as those needed for efficient waste heat energy conversion or direct thermal-to-electrical power plants. In order to overcome this challenge, we are using an alternative energy conversion approach which utilizes thermionic carrier transport in metal/semiconductor superlattices composed of materials that are stable at high temperatures[ref 1,ref 2]. In this case, even though the individual layers may not have attractive thermoelectric properties, the suppression of the cross-plane thermal conductivity due to the high interface density combined with the enhancement in the power factor arising from energy filtering are expected to yield effective ZT values that exceed the ZT of the best high temperature bulk materials (~ZT = 1). We have identified and explored TiN/GaN and ZrN/ScN as two possible metal/semiconductor combinations for thermionic energy conversion. The selection of the materials was constrained by issues that are critical to the integration of heterogeneous materials such as crystallographic compatibility and thermodynamic stability of the metal/semiconductor combinations at high operating temperatures. The first nitride superlattice system consists of TiN as the metal layer and GaN, in its metastable rocksalt phase, as the semiconductor layer, grown on rocksalt MgO substrates. The metastable rocksalt GaN (rs-GaN) phase is stabilized by pseudomorphic epitaxy on a metallic rocksalt TiN underlayer, and its existence has been verified using high-resolution x-ray diffraction and transmission electron microscopy. The critical thickness for the rocksalt-to-wurtzite phase transition has been empirically determined to be between 1 and 2 nm, although much thicker rocksalt GaN films, up to approximately 6 nm, can be maintained for several superlattice periods. The second pure rocksalt-structured superlattice system analyzed consists of alternating layers of metallic ZrN and semiconducting ScN. These epitaxial superlattices were grown on rocksalt MgO substrates using dc magnetron sputtering in a nitrogen-argon ambient. The structural, electrical and thermal properties of these two metal/semiconductor superlattice systems will be presented in detail, along with a discussion on the suitability of these materials for high temperature direct thermal-to-electrical energy converters. [1] Mahan et. al., Phys.Rev.Lett. (1998). [2] Shakouri et. al. Appl.Phys.Lett.(1997).

4:00 PM U8.8

Carrier Transport Behavior of Thermoelectric $Ca_{0.32}CoO_2$ Epitaxial Films with Different Ca-Ordering Structure. Kenji Sugirua[1], Hiromichi Ohta[1,2], Yukiaki Ishida[3], Kenji Nomura[4], Masahiro Hirano[4], Hideo Hosono[4,5,6] and Kunihito Koumoto[1,2]; [1]Graduate School of Engineering, Nagoya University, Nagoya, Japan; [2]CREST, Japan Science and Technology Agency, Saitama, Japan; [3]RIKEN/SPring-8, Hyogo, Japan; [4]ERATO-SORST, Japan Science and Technology Agency, Yokohama, Japan; [5]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [6]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan.

Here we report metal/insulator transition like carrier transport properties of a layered cobalt oxide, $Ca_{0.32}CoO_2$, which have two different Ca-ordering structure of √3a ×√3a hexagonal (hereafter "type H") and 2a × √3a orthorhombic (hereafter "type O") types. Na_xCoO_2 exhibits several unique electron transport behavior such as fairly large thermopower (x~0.7), insulating nature (x~0.5), and superconductivity (x~0.3) by changing Na concentration, x. Although Na-ion ordering structure [1] may play a key role for electron conduction in Na_xCoO_2, this is still mysterious because of the chemical instability of Na_xCoO_2. We chose Ca_xCoO_2 to clarify the unique carrier transport behavior because Ca-based cobalt oxide is much chemically stable as compared to Na-based one. Further, we have found that high-quality Ca-Co-O epitaxial films can be easily obtained by topotactic ion-exchange of R-SPE grown $Na_{0.8}CoO_2$ epitaxial film [2,3] though bulk single crystal of Ca-Co-O is considered to be very difficult to obtain. First, high-quality epitaxial films of $Ca_{0.32}CoO_2$ with type H structure were prepared by the ion-exchange treatment of the R-SPE grown $Na_{0.8}CoO_2$ film with $Ca(NO_3)_2$ powder. On the other hand, the type O films were prepared by simple thermal annealing of type H film at 300~400°C. Typical metallic conductivity was obtained in the type H film. The resistivity increased proportionally to T^2 below ~ 140 K likely due to electron-electron interaction while it was saturated (~ 10^{-3} Ωcm). Thus, degenerate Fermions dominate the carrier conduction below 140 K though electron hopping is dominant above 140 K. On the other hand, type O film exhibited typical semiconducting behavior. The slope of log σ - T curve was proportional to -1/3 below ~300 K, suggesting that the variable-range hopping (VRH) conduction is dominant at low temperatures, while it was -1 above ~300 K, suggesting that the nearest-neighbor hopping (NNH) conduction is dominant at high temperatures. Although the occupancy of Ca-site in type H structure is 100%, that in type O is only ~60%. Such Ca-vacancy may affect valance of Co to form potential barrier, resulting in weakly localization of carrier. The present results clearly demonstrate that cation ordering structure of Ca_xCoO_2 affect not only crystallographic symmetry but also electron transport significantly.

[1] M. Roger *et al.*, *Nature* **445**, 631 (2007).
[2] H. Ohta *et al.*, *Cryst. Growth Des.* **5**, 25 (2005).
[3] K. Sugiura *et al.*, *Appl. Phys. Lett.* **89**, 032111 (2006).

4:15 PM U8.9

Thermoelectricity in La-doped Strontium Titanate Thin-films. Choongho Yu[1], Matthew Scullin[2,1], Mark Huijben[3], Subroto Mukerjee[3], Joe Feser[4], Joel Moore[3,1], R. Ramesh[2,1] and Arun Majumdar[4,1]; [1]Materials Sciences, Lawrence Berkeley National Lab, Berkeley, California; [2]Materials Sciences and Engineering, Univ. of California, Berkeley, California; [3]Physics, Univ. of California, Berkeley, California; [4]Mechanical Engineering, Univ. of California, Berkeley, California.

Recent works have shown that La-doped SrTiO3 (SLTO) is promising for thermoelectricity since its power factor is comparable to that of Bismuth tellurides. During the pulsed laser deposition of La-doped SrTiO3 (STO), it is very difficult to prevent oxygen deficiency in both the SLTO film and the lattice-matched STO substrate that it is grown on. Oxygen deficiency increases the electrical conductivity of the film, thus affecting power factor. Furthermore, it makes the STO substrate conductive, which complicates the measurements of SLTO film properties. This paper presents a systematic study of oxygen deficiency on both the film power factor and substrate contribution. In addition, this paper investigates the role of defects on thermal conductivity reduction, which has a significant impact on the thermoelectric figure of merit.

4:30 PM U8.10

Vacuum Thermionic Energy Conversion from Nitrogen and Phosphorus Doped Diamond. Joshua Ryan Smith[1], Robert J. Nemanich[2] and Griff Bilbro[3]; [1]Department of Physics, North Carolina State University, Raleigh, North Carolina; [2]Department of Physics, Arizona State University, Tempe, Arizona; [3]Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina.

A vacuum thermionic energy conversion device can potentially convert heat directly to electrical work in an efficient manner. One aspect that limits the performance of TEC devices is the negative space charge which develops in front of the emitter surface. Furthermore, materials with moderate work functions (>3eV) have required high emitter temperatures (2000K) to produce appreciable power. Hydrogen terminated, doped diamond features a negative electron affinity (NEA) which can mitigate the negative space charge effect in the TEC. Moreover nitrogen and phosphorus doped diamond can result in surfaces with a low work function and a lower emission barrier then conventional thermionic materials. In this study, a theory was developed to model the electron transport across a TEC featuring an NEA material as the emitter electrode. The efficiency is calculated by considering energy transport via thermionic electrons and Stefan-Boltzmann radiation. Two TEC designs were modeled: one with characteristics of a nitrogen doped diamon